NUTRIENT RECOVERY AND MANAGEMENT IN FULL SCALE WASTEWATER TREATMENT PLANTS: FEASIBILITY AND OPTIMIZATION

by

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ABSTRACT

Recovering and recycling nutrients from wastes has been a major research component in environmental engineering over the past 20 years. Advanced industrial technologies followed by excess human consumption lead to the release of higher concentrations of reactive organic and inorganic nutrients to surface water bodies leading to major environmental concerns such as eutrophication, algal blooms, etc. (Edwards et al., 2000). Besides, large amounts of nutrients present in waste streams pose a critical problem with regards to wasting and depletion of phosphorous at a significant rate. As municipal wastewater treatment plants (WWTPs) are one of the potential sites of nutrient deposition, recovering and recycling excess nutrients and closing the nutrient loop that would otherwise be discarded offers economic as well as environmental benefits. Furthermore, the depletion of natural phosphorous resources and the implementation of much stringent regulations are becoming major issues for many WWTPs and are currently emphasizing nutrient recovery and management.

In this study a series of bench top experiments were conducted to recover nutrients through chemical precipitation. Local municipal wastewater treatment plants were considered as model systems for this study. For one set of samples, nutrient recovery was tested for addition of different chemicals (i.e., sodium hydroxide (NaOH), magnesium hydroxide ($Mg(OH)_2$), magnesium chloride ($MgCl_2$)) at a controlled pH ranging from 8–10 to recover them in the form of struvite. For the other set of samples, effect of pH and temperature were studied on struvite recovery. In addition, to compare the recovery of

nutrients in a wide range, samples were collected from diverse WWTPs containing different treatment technologies (i.e., trickling filter process, trickling filter/solids contact (TF/SC) process and enhanced biological phosphorous removal (EBPR)). Samples were collected at different times of the year to account for the varied seasonal changes and the working conditions at the WWTPs. Proportions of chemicals added and the pH maintained were optimized for each sample to achieve maximum recovery. Up to 85–90% of phosphorous and 25% of nitrogen recovery has been observed in the experiments, performed under different conditions. Maximum recovery was observed at a ratio of NH_4:PO_4^{3-+}:Mg^{+2} 1:1:2 to 1:1:1.3. Among all the samples tested, filtrate samples had the highest nutrient recovery potential.

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CHAPTER I

INTRODUCTION

Nutrients in the environment

Nutrients are substances central to the function and growth of organisms and are present everywhere. In our natural ecosystems, nutrients get transformed into different organic and inorganic forms in the presence of various biotic and abiotic conditions. Of all the nutrients present, nitrogen (N) and phosphorous (P) are of major concern in wastewaters as they are potential pollutants and can accelerate the eutrophication of lakes and reservoirs, stimulate the growth of algae in shallow streams, create low dissolved oxygen (DO) conditions which endanger aquatic life. With high demographic and industrial development, discharge of reactive inorganic nitrogen and phosphorous from point and nonpoint sources to natural waters is increasing. In the U.S., the mass of nutrients entering waters has increased significantly over the past 5 decades, and nutrient pollution now poses a serious nationwide water quality concern (Selman et al., 2008; EPA, 2009).

Nitrogen

Nitrogen is a critical nutrient required in the growth of all organisms. Organic nitrogen is found in a variety of biological substances, such as peptides, proteins, enzymes, chlorophylls, energy transfer molecules (ADP, ATP), and genetic materials RNA, DNA (Barsanti and Gualtieri, 2006). Nitrogen as a nutrient plays an important role in our environment; however, when present in excess quantities, reactive nitrogen causes a range of

negative environmental effects, poses risks to human health, and can result in adverse economic and social consequences. Significant concentrations of nitrogen can lead to depletion of dissolved oxygen in receiving waters, toxicity to aquatic life, adverse impact on chlorine disinfection efficiency, groundwater and soil pollution, creation of a public health hazard, and wastewater that is less suitable for reuse (Correll, 1998; Daniel et al., 1994; Edwards et al., 2000; Jackson and Lawrence, 1998; Kruger et al., 1995; Sims et al., 1998).

Atmospheric nitrogen is converted to ammonia by the action of bacteria (Genus Rhizobium, Cyanobacteria) in soil called "nitrogen fixation" producing reactive forms of nitrogen. Thus, nitrogen is a renewable source and can be fixed in the environment. In wastewaters, nitrogen is mostly present in soluble inorganic N-species ($NO_{3-,}$ NO_{2-}, NH_4^+, NH_3). Nitrogen is removed through nitrification and denitrification biological processes in the wastewater treatment. Ammonia is a common pollutant of water and toxic to aquatic life. It is regulated by the wastewater treatment plants and is conventionally treated using nitrification and denitrification processes in the system. Though complete theoretical nitrogen removal is anticipated in the treatment process, in reality it is difficult to achieve an actual nitrogen mass balance due to different bacterial communities present in the system. Among the two processes, nitrification is the controlling reaction as ammonia oxidizing bacteria lack functional diversity, have stringent growth requirements, and are sensitive to environmental conditions (Jeyanayagam, 2005). Significant loss of nitrogen is observed. Secondary treatments are applied to reduce the effluent concentrations to meet the national pollutant discharge elimination system (NPDES) permit. Nitrate, nitrite concentrations are regulated in wastewater effluents to avoid eutrophication issues in receiving waters and potentially contaminating adjoining drinking water resources.

Phosphorous

Phosphorus (P) is of fundamental importance to living things and is an essential nutrient for crop production. It is an irreplaceable element in many physiological and biogeochemical processes. It is widely used for agriculture purposes, insecticides, and detergents, finally accumulating in waste waters. It is one of the major components of the agriculture industry and thus it is indirectly connected with the global food industry. Excess concentration of phosphorous causes severe eutrophication and algal blooms in surface waters. Thus, many countries have implemented stringent nutrient management regulations that reduces the discharge of nitrogen and phosphorous into the surface waters. Phosphorous in wastewaters is generally treated using enhanced biological phosphorous removal processes (EBPR) to reduce the final effluent concentrations to a low range of 0.05–0.1 mg/l or even lower concentrations. The conventional phosphate removal technique applied for the wastewater treatment is based on phosphate fixation in activated sludge. The processes unfortunately generate huge amounts of a water-rich sludge which has to be disposed of at continuously increasing costs.

Concerns of excess nutrients

Eutrophication is the excess growth of algae as a result of excess nutrients (particularly N and P compounds) in surface waters, such as rivers, lakes, and seas (Bashan and Bashan, 2004). It can be observed as a consequence of over fertilization of aquatic environments due to human actions, or it can be a natural phenomenon where the seasonal increase in nutrients causes the organic load in a lake to increase (Doyle and Parsons, 2002). Generally, phosphorous is the limiting nutrient and is seen as the major nutrient responsible for eutrophication. There are many negative effects associated with eutrophication of water bodies, which includes increased biomass of phytoplankton, oxygen depletion, increased

incidence of fish kills, and loss of desirable fish species; decreases in perceived aesthetic value of the water body, and taste, odor and water treatment problems (Carpenter et al., 1998). Severe eutrophic conditions have already been widely experienced and reported in various places around the world (eg. Chesapeake Bay, Great Lakes, European countries, China etc.). To safeguard the water bodies and the ecosystems associated with them, The Environmental Protection Agency (EPA) and European Commission's Urban Wastewater Treatment Directive (UWWTD) has implemented strict regulations to reduce the concentrations of nitrogen and phosphorous entering the surface waters and coastal lands in many countries.

Global scenario of phosphorous

Phosphorus is generally obtained from the phosphate rock in the form of apatite through mining operations which are limited to only a few places in the world. It is a nonrenewable source, and excess exploitation of natural geological resources is leading to depletion of natural resources. It is indispensable and furthermore, there is no substitute for phosphorus in nature (USGS, 2005). In the present scenario, depletion is not the only concern for phosphorous resources; the major concern is the decreasing quality of phosphorous rocks (Chambers et al., 2001). Phosphorous mining is challenged by the quality of phosphorous rock and increased concentrations of heavy metals like Cadmium (Cd) and Nickel (Ni). These impurities make the use of phosphorous rocks unacceptable as they require higher energy and treatment processes to remove the heavy metals present.

Mining of phosphorous ores is mostly concentrated in North Africa, Morocco, China and the United states. With the global demand for phosphorous increasing annually, it is estimated that there are only 7000 million tons of phosphate rocks as P_2O_5 remaining in these reserves that could be economically mined. This decrease in the availability of natural

phosphorous reserves has affected its commercial prices in the market. Recently the United States Geological Survey (USGS, 2008) has reported that prices have increased by 800 times. Furthermore, the human population consumes 40 million tons of phosphorous as P_2O_5 each year (Florida Institute of Phosphate Research, 2005; Steen, 1998; Jasinski et al., 1999). It is predicted that phosphorous demand will increase by 1.5% each year (Steen, 1998). It will be highly difficult and competitive to maintain the balance between the demand and supply of phosphorous resources due to increasing global need. As an alarming fact, it has been hypothesized that phosphate rock production might "peak" in the years 2033 or 2034, and then fertilizer production would unavoidably decrease as reserves are depleted. (European Fertilizer Manufacturers Association, 2000).

Challenges with biological and chemical nutrient removal processes

Conventional waste water treatment includes removal of organics, biological oxygen demand (BOD), chemical oxygen demand (COD), and nutrients. The activated sludge process is one of the most common treatment methods for municipal wastewaters due to its ability to produce high effluent quality, nitrification rates and COD removal. It is generally used to treat ammonia-nitrogen to nitrate-nitrogen via the biological process–nitrification. But this process often results in production of excess sludge, increased costs of aeration (Grady et al., 1999). For treatment plants with longer SRTs, filamentous bulking can also be a major drawback. Much research has already been done to modify the conventional activated sludge process and enhance the nutrient removal by adding or by making different configurations such as by providing mixed, non-aerated zones and internal process recycle streams to create the anoxic or anaerobic environments required for biological nitrogen and biological phosphorous removal, respectively (Grady et al., 1999).

Nitrification and denitrification are the major processes for nitrogen removal. Ammonia is converted to nitrite and then into nitrate in oxic conditions by the ammonia oxidizing bacteria AOBs. During denitrification, nitrate is reduced back to dinitrogen gas in anoxic conditions and requires a readily biodegradable organic source as food for the microorganisms. Removal of total nitrogen (TN) from the treatment system is drawing a lot of attention due to stringent discharge regulations. Denitrification is proposed as a solution to achieve it, but it leads to high emissions of nitrous oxide. This gas has a global warming potential approximately 300 times greater than that of carbon dioxide (Burrowes et al., 2007). Phosphorous is removed via Enhanced biological phosphorous removal i.e., luxurious uptake of phosphorous by aerobic heterotrophs (PAOs) capable of storing orthophosphate in excess of their biological growth requirements. They store polyphosphate as an energy reserve in intracellular granules. Under anaerobic conditions, in the presence of fermentation products, PAOs release orthophosphate. Under aerobic conditions, the PAOs then grow on the stored organic material, using some of the energy to take up orthophosphate and store it as polyphosphate (Strom, 2006a, 2006b).

Biological nutrient removal (BNR) process configurations have been studied extensively in wastewater to achieve low levels of nutrients in the discharge effluents. BNR configurations vary based on the sequencing of environmental conditions (i.e., aerobic, anaerobic, and anoxic) and timing (Metcalf and Eddy, 2003). They can be either TN removal or TP removal or both depending upon effluent quality, operator experience, influent quality, and existing treatment processes (if retrofitting/integrating an existing facility for enhanced nutrient removal). Wastewater treatment plants are integrating/retrofitting biological nutrient removal technologies to the conventional treatment chain to meet the effluent limits. Recently, more stringent regulations on nutrient discharge to water bodies

have brought about the growth and real time implementation of several biological nutrient removal plants throughout the world. Some of the major BNR process configurations are Ludzack–Ettinger process, Balakrishnan and Echeknfelder, modified Ludzack–Ettinger process (MLE), A^2/O (anaerobic, anoxic, oxic) process, step feed process, Bardenpho process, sequencing batch reactors (SBR), rotating biological contactor (RBC) process, and oxidation ditches.

However, increasingly sophisticated means of BNR processes come at a cost of higher resource consumption (e.g. energy, chemicals, and infrastructure) and result in producing large amounts of nutrient rich sludge which is a major drawback. BNR processes also involve greater pumping of recycle streams to the anaerobic and anoxic stages. Pumps and air blowers are the largest energy consumers in wastewater treatment. Operating real time BNR system and simultaneously handling the sewage sludge is a challenge in wastewater treatment in terms of safe guarding the environment. Shizas and Bagley (2004) showed experimentally that sewage contains ten times the energy needed to treat it. Such interest has shifted the view of municipal sewage from a waste to be treated and disposed of, to a resource that can be processed for recovery of energy, nutrients or other constituents. In recent years, side stream processes to treat the sludge are gaining a lot of interest as such produces can produce energy, recovery of nutrients or biogas as a byproduct (Hallenbeck., 2005 and Gong et al., 2005). Side stream processes can be physical, chemical, biological or thermal processes to treat sludge. Of all the existing technologies, anaerobic digestion has become the benchmark method for treating sewage solids. Anaerobic digestion reduces the excess biomass by 40–50 % along with biogas production as a byproduct (Balmér, 2004). There is a high potential for recovering and recycling nutrients if proper side stream technologies are applied.

Another common practice of treating phosphorous is by adding chemicals. Salts of iron, calcium, and aluminum are often added to precipitate phosphorous by forming their respective phosphate precipitates. This chemical treatment helps in reducing BOD, organics and TSS in the system but often leads to excess sludge production of up to 10–25% actual biomass production. This can be dramatic, especially if the method selected is lime application during primary treatment (Tchobanoglous et al., 2003). Use of alum after secondary treatment can be predicted to produce much less sludge, but the increase could still be problematic (Strom, 2006a). Katehis et al. (2003) found that higher concentration of iron salts form vivanite ($Fe_3PO_4.8H_2O$) in the digesters hindering struvite formation. Excessive usage of iron salts can drop the pH of the system during anaerobic digestion leading to corrosion of the digestion and post digestion infrastructure (Earth Tech et al. 2002).

Sources of phosphorous and its uses

Phosphorus is used mainly in the agricultural industry followed by use in commercial and industrial products. The main distinguishing feature between the two sectors is the relative purity of their products. Agricultural use is mainly focused on manufacture of fertilizers, which requires little purification. As crops need other minor nutrients to grow, presence of other substances to some extent is allowable. The industrial sector manufactures high purity phosphates for a variety of industrial applications, including detergents, water treatment, flame retardants, paints, pharmaceuticals, beverage, and food uses (Driver et al., 1999; Morse et al., 1998).

Phosphorus can enter water bodies from industrial, human, and agricultural sources, generally classified as either point or nonpoint sources. Point sources such as human excretions, sludge generated from wastewaters and its effluents, livestock intensification, and

beverage industries; tend to have continuous discharge with little variation over time (Carpenter et al., 1998). If these point sources are properly managed and treated, substantial amount of nutrients can be reduced entering the water bodies. Although nonpoint sources can also have continuous inputs, they are more often intermittent and dependent on seasonal activities such as agriculture (excessive fertilizer use), surface runoff or major construction. Since nonpoint sources can cover a large area and be transported overland or underground to receiving waters, they are difficult to monitor and control, and consequently nonpoint inputs are the major source of water pollution in the United States (Carpenter et al., 1998).

Advantages of phosphorous recovery

As discussed, sewage solids have high concentrations of nutrients, organics, and pathogens present in them. It is estimated that sewage sludge contains at least 25% of the phosphorus that is present in raw wastewater (WERF, 2005). Incinerating sludge is highly uneconomical due to increasing energy costs and constraints (fuel cost, ash treatment, GHG emissions) associated with it. Land application of biosolids is restricted in many states due to health risks and environmental concerns owing to potentially high pathogenic or heavy metals/toxic substances in the sewage sludge (Wei et al., 2003). Anaerobic digestion helps in reducing excess biomass as well as generates biogas (methane) and produces a nutrient rich liquid called filtrate; which is recycled in the plant. It is found that recycling of filtrate can increase the nutrient loading to incoming wastewater by 30% (Pastor et al., 2008). It requires that the on-going biological treatment process must be designed for this additional nutrient load coming in. Recovering these nutrients can reduce the slug load coming into the plant and enhance the biological operations. It can also help reduce the final nutrient concentrations entering the surface waters. Treated sewage solids can be applied to

agricultural lands after digestion processes; thereby reducing the volume of solids which would otherwise be dumped into landfills.

Recovering the nutrients in the form of struvite could be beneficial as it produces a value added product. Furthermore, revenue generated from struvite recovery may help off-set the cost of meeting nutrient discharge regulations. Struvite produced from the crystallization process is of higher purity in terms of phosphorous content than the natural source of mined phosphorous rocks; which makes it more attractive to recover. Besides, the process is well suited for wastewaters with concentrated nutrients (Dempsey, 1997). Theoretical composition of struvite on a weight basis is about 9.9% magnesium, 5.7% nitrogen, and 12.6% phosphorus with the remainder being crystalline water. Struvite removal is the only process that enables removal of a significant amount of ammonia versus recovering it in the form of its corresponding phosphates.

Some of the agricultural studies have proven that struvite is a very good slow release fertilizer, which contains higher percentage of bio available phosphorous to crops, and it can outcompete conventional fertilizers for better crop production (Johnston and Richards, 2004). Struvite satisfies a need for mineral slow-release fertilizers and has potential uses in horticulture, for nurseries, golf courses, etc. Recovered struvite can be considered as a secondary raw material, not a "waste". It can be used as a potential raw material to supplement phosphorous industry.

These advantages of phosphorous versus its global depletion scenario make it interesting to study. Nutrient-rich waste sludge can be recovered into a value added product and reused, there by closing the nutrient loop.

CHAPTER II

RESEARCH OBJECTIVES AND TASKS

As mentioned above, wastewater consists of different kinds of organic and inorganic compounds of anthropogenic and natural origin. Presence of excess nutrients, especially Nitrogen and Phosphorus in wastewater discharges and their impacts on natural water bodies are of major concern. Implementations of advanced biological nutrient removal technologies are efficiently reducing the final effluent concentrations but results in producing concentrated, nutrient rich sludge (Doyle and Parsons, 2002). With limited areas of land being available for landfilling; treating this excess sludge could be very expensive and energy, labor intensive (Barjenbruch and Kopplow, 2003). If the nutrients present in side stream processes are recovered, then sludge handling problems and final nutrient discharge limits may be met. Thus, I chose to study one of the nutrient recovery methods, (i.e. "*struvite precipitation"* from side stream (nutrient-rich) sludge processes as my research topic). There are several physical and chemical techniques to recover nutrients, but struvite crystallization promises to be a reliable method and has immediate benefits which make its study more interesting.

Struvite formation is considered as one of the major operational setbacks often observed in digestion and post digestion processes at wastewater treatment plants. But forcing controlled struvite precipitation can recover ammonia (NH_4-N) and phosphorous (PO_4-P) in the presence of favorable pH and an external magnesium source as a precipitate

that can be re-used. In this approach, nutrient load reductions in recycle loads eliminate nutrient accumulation issues in WWTPs (e.g., struvite scaling, production of phosphorous rich biosolids that are ineligible for land application, etc.) as well as facilitate savings through reduced aeration requirements. Incorporating nutrient removal systems in side stream processes can efficiently recover the excess nutrients from digested sludge. Besides, global demand for 'phosphorous' in agriculture and the food industry is increasing at an astounding rate due to rapid urbanization. Struvite precipitation can counterbalance this natural resource crisis with management of nutrient rich sludge by producing a value added fertilizer. It can be marketed to offset the installation and operating costs and also helps to reduce the nutrient load coming to the plant.

Generally, phosphorous is also recovered in the form of calcium phosphates, which can be used as a raw material for phosphorous inclusive purposes; but struvite is a sole product which can simultaneously reduce recycled phosphorous and nitrogen loads to the plant. With depletion of natural resources and implementation of more stringent regulation on nutrient discharges becoming a major issue, WWTPs are now emphasizing on nutrient recovery and management.

Theoretically, equimolar concentrations of ammonium, phosphorous, and magnesium are sufficient to precipitate struvite under favorable physical conditions. However, until practical evaluation is undertaken into the recovery process the true feasibility cannot be established. To analyze the actual economic feasibility of nutrient management in the form of struvite, a full scale quantitative evaluation is necessary (Wu et al., 2004). This research helps to evaluate the feasibility of recovering nutrients through chemical precipitation by considering local municipal WWTPs (with different treatment technologies) as model systems and suggests nutrient management solutions to these

treatment plants. Thus I have considered the following research objectives and tasks to accomplish the corresponding objectives.

Objectives

(1) To investigate the feasibility of recovering nutrients from anaerobic digestion and post digestion liquors in the form of struvite at a laboratory scale.

(2) To develop nutrient removal and recovering strategies considering local MWWTPs as model systems.

Tasks

To accomplish these research objectives, the following tasks were performed.

(1) Collect the mixed liquor samples from different WWTPs seasonally and characterize the baseline concentrations of nutrients and metals present in them.

(2) Conduct nutrient recovery tests by varying the chemicals added at a controlled pH range.

(3) Optimize the experimental conditions for all the samples to achieve maximum nutrient recovery.

(4) Develop nutrient recovery and management strategies for different treatment plants in terms of cost effectiveness and adaptability.

CHAPTER III

LITERATURE REVIEW

Struvite Occurrence

Accumulation of struvite ($MgNH_4PO_4.6H_2O$) on pipe walls and equipment surfaces of anaerobic digestion and post-digestion processes is a problem that plagues the wastewater treatment industry. Remediation is often impractical and even if possible, it is costly in terms of labor, materials, and systems downtime (Ohlinger et al, 1998). Presence of equimolar concentrations of ammonia, phosphorous, and magnesium under favorable conditions can lead to struvite formations. The initial buildup of struvite on the walls creates suitable surfaces for further struvite formation; gradually small crystals attach to the suspended particles in sludge and on surface of the equipment and pipe walls of the system and leads to struvite formation (Borgerding, 1972). Crystal growth due to constant supply of nutrients under favorable conditions can be rapid, and if left unchecked, struvite accumulation can foul and clog within (Westerman et al., 1985; Suzuki et al., 1989).

Struvite crystallization was studied by Rawn in 1939 and first observed at the Hyperion WWTP in Los Angeles in the 1960s leading to severe operational problems at the site. In treatment plants, struvite formation can cause capacity loss by compromising process control and negatively affect the performance of the sludge and filtrate conveyance system (Benisch et al., 2002).

Formation of struvite

Struvite precipitation has been extensively studied due to the need to prevent struvite from forming on the walls of pipes and pumps in municipal wastewater treatment plants. Wastewaters have a complex matrix consisting of dissolved nutrients, solids, metals, and other inorganics. As the water is treated these organics are broken down by microbes by taking up the nutrients, which act as food for microorganisms. During anaerobic digestion, nutrients (ammonia and phosphate) are released again as part of the volatile solids destruction (Miles and Ellis, 2001). The series of steps that lead to struvite precipitation in the digesters include phosphorous solubilization, intracellular magnesium release, loss of carbon dioxide into gas phase, subsequent increase of pH, and shift in equilibrium towards orthophosphate and ammonia, forming struvite nucleation and crystal growth (Ohlinger et al., 1998).

Concentrations of the nutrients released mainly depend on the treatment technology used for its treatment. To precipitate phosphorous, the phosphorous must be available as soluble phosphate (also referred to as orthophosphate). Organically bound phosphorous can be converted to orthophosphate in anaerobic treatment processes as well as in other biological processes. Large amounts of ammonia are released as bacterial cell composition consists of 6–7% of nitrogen and also 2–3% of phosphorous by weight. Ammonia concentration in the bulk fluid increases significantly as proteins are degraded and dissolved magnesium and phosphate concentrations increase due to cell lysis (Sen et al., 1988). For conventional wastewater treatment plants, the concentrations of magnesium are largely influenced by the service area water supply. The pH of anaerobic digestion and post-digestion processes is generally higher than the pH of preceding treatment processes; hence, struvite precipitation potential is greater in digestion (Munch and Barr, 2000).

Struvite chemistry

Struvite, also chemically known as magnesium ammonium phosphate (MAP), is formed when equimolar concentrations of its ionic constituents are present in concentrations greater than its solubility product. Struvite crystals are usually stable, white, and orthorhombic in shape (Le Corre et al., 2005). Struvite formation is a crystallization process and depends on the pH, ionic strength of individual ions and temperature of the system.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \quad (1)$$

Struvite formation generally occurs in two stages: nucleation and crystal growth. Nucleation occurs when ions combine to form crystal surfaces that act as the foundation for growth into detectable crystals. Crystal growth continues until respective component ions reach their equilibrium or attain supersaturation. In systems having a constant supply of struvite constituents, crystal growth continues indefinitely. Predicting or controlling these mechanisms is a complex process since they are controlled by a combination of physical–chemical parameters. Super saturation of ions in a solution is a key parameter leading to crystallization, which in turn depends on solution pH and reactive solution concentration. Struvite precipitates when the concentrations of the constituent ions become supersaturated in the solution (Doyle and Parsons, 2002). Supersaturation occurs when the point of solubility is exceeded by the individual ions. Solubility product is calculated as follows:

$$[NH_4^+]\,[PO_4^{3-}]\,[Mg_2^+] = K_{sp}\ \text{struvite} \quad (2)$$

For dilute solutions, the ionic strength correction is small enough to ignore, resulting in the above equation. The rate at which struvite forms and dissolves in the reactor is an important parameter with regards to phosphorus recovery. If the product of the concentrations of constituent ions in solution exceeds the equilibrium solubility of struvite,

struvite will form; if the product is lower than the equilibrium solubility, struvite will dissolve. Many studies have been undertaken to determine the solubility product of struvite (Abbona et al., 1982; Ohlinger el al., 1998; Stumm and Morgan, 1981; Snoeyink and Jenkins, 1980; Taylor et al., 1963; Webb and Ho, 1992) as shown in Table 1. The tests were usually conducted in distilled water or in waste water samples under controlled conditions of pH, temperature, and mixing energy (Burns and Finlayson, 1982; Bouropoulos and Koutsoukos, 2000; Ohlinger et al., 1998). After the solution is assumed to be in equilibrium with its corresponding ions, the solubility product is determined by analyzing the ionic concentrations.

Different pK_{sp} values are due to the inclusion of complexes formed in solution and the chemical speciation determined was different for various authors (Doyle and Parsons, 2002). A number of chemical equilibrium based models have been developed to understand the prediction of struvite precipitation (Musvoto et al., 2000). MINTEQA2 modeling was used in conjunction with laboratory studies to predict the potential for struvite precipitation as a function of pH and magnesium, ammonium, and phosphate molar ratio.

Thermodynamic equilibrium reactions for different complex intermediate compounds formed during struvite crystallization are

$$K_{MgOH+} = \frac{\{Mg^{+2}\}\ \{OH^{-}\}}{\{MgOH^{+}\}} \quad (3)$$

$$K_{NH4}{}^{+} = \frac{\{H^{+}\}\ \{NH_3\}}{\{NH_4{}^{+}\}} \quad (4)$$

$$K_{HPO4}{}^{2-} = \frac{\{H^{+}\}\ \{PO_4{}^{3-}\}}{\{HPO_4{}^{2-}\}} \quad (5)$$

$$K_{H2PO4}{}^{-} = \frac{\{H^{+}\}\ \{HPO_4{}^{2-}\}}{\{H_2PO_4{}^{-}\}} \quad (6)$$

$$K_{H3PO4} = \frac{\{H^{+}\}\ \{H_2PO_4{}^{-}\}}{\{H_3PO_4\}} \quad (7)$$

$$K_{MgH2PO4}^{+} = \frac{\{Mg^{+2}\}\ \{H_2PO_4^{-}\}}{\{MgH_2PO_4^{+}\}} \quad (8)$$

$$K_{MgHPO4} = \frac{\{Mg^{+2}\}\ \{HPO_4^{2-}\}}{\{MgHPO_4\}} \quad (9)$$

$$K_{MgPO4}^{-} = \frac{\{Mg^{+2}\}\ \{PO_4^{3-}\}}{\{MgPO_4^{-}\}} \quad (10)$$

The sum of the ionic concentrations of the free ions and complexes of the constituent ions (Mg_2^{+}, NH_4^{+}, and PO_4^{3-}) can be expressed as the following total soluble constituent species concentrations (Ali and Schneider, 2008; Bouropoulos and Koutsoukos, 2000; Wu and Bishop, 2004). The solution thermodynamic properties described below specify the state of saturation, free ion concentrations, and the state of precipitation. Precipitation of struvite occurs in supersaturated solutions, which is particularly influenced by the pH of the solution and the reactant concentrations.

$$C_{T,NH4} = [NH_3] + [NH_4^{+}] \quad (11)$$

$$C_{T,Mg} = [Mg^{2+}] + [MgOH^{+}] + [MgH_2PO_4^{+}] + [MgHPO_4] + [MgPO_4^{-}] \quad (12)$$

$$C_{T,PO4} = [H_3PO_4] + [HPO_4^{-}] + [HPO_4^{2-}] + [PO_4^{3-}] + [MgH_2PO_4^{+}] + [MgHPO_4] + [MgPO_4^{-}] \quad (13)$$

Fluidized bed reactors (FBR) or air-agitated reactors are the most commonly used processes for crystallizing struvite from wastewater. The geometry of these reactors is such that the flow velocity will decrease upwards, allowing treated effluent to flow out the top of the reactor while the growing particles remain in the lower section. Fluidization of the particles is achieved through either the liquid flow rates with feed entering the reactor column from the bottom (Mangin and Klein, 2004), or the up-flow circulation of air that keeps growing particles from settling down (Le Corre et al., 2009). Reactors are seeded to achieve better agglomeration of particles, and chemicals are added at the bottom of the reactor, which are mixed and circulated through aeration. Struvite pellets are recovered from the bottom of the reactor when they reach an acceptable size. Challenges in implementation

and maintenance of these processes are the cost of raw materials as well as the energy requirements for keeping the seedbed fluidized (Le Corre et al., 2009).

Factors affecting struvite precipitation

Struvite crystallization occurs when equimolar concentrations of its ionic constituents exceed its solubility product. Crystallization process is greatly influenced by factors like pH, temperature, mechanical mixing, presence of other metal ions, Mg:P ratio, and seeding of the reactor.

pH

The pH level of the solution impacts the amount of these parameters in the NH_4^+, PO_4^{3-}, and Mg^{2+} forms needed to exceed the struvite solubility product and cause struvite to precipitate. It is observed that the struvite is highly soluble at acidic pH and highly insoluble at alkaline pH. When the pH increases, the orthophosphate concentration increases, whereas the magnesium and ammonium concentration decrease. Each of the ions that make up struvite will also form other complexes, both with each other and with hydrogen and hydroxide ions (Bhuchanan et. al, 1994). Previous studies showed that a pH increase from 7–9, causes the percent of total ammonia nitrogen present as NH_4^+ to decreases from 99% to 64% and similarly, the fraction of total PO_4-P present as the PO_4^{3-} anion increases 250-fold (Stumm and Morgan, 1970). Thus the excess concentration of total orthophosphorous (PO_4^{3-}) in the solution has a greater influence on struvite precipitation than does the pH effect on NH_4^+ activity.

Temperature

Temperature affects both the equilibrium position of a precipitation reaction and the reaction rate to some extent. In general, solubility increases with increasing temperature.

Previous studies suggest different opinions on the effect of temperature on solubility of struvite. Durrant et al. (1999) reported that the maximum solubility occurred at 20°C and Bhuiyan et al., 2007 reported that maximum solubility occurs at 35°C. A similar study conducted by Aage et al. (1997) found that the maximum solubility was at 50°C. Doyle and Parsons (2002) found that at high temperatures, the structure of struvite pellets changed, which affected their solubility. Ideally, struvite precipitation can be achieved at standard temperatures with recovery of up to 95% (Snoeyink and Jenkins, 1980).

Mg:P molar ratio

Magnesium is often considered to be the limiting parameter in wastewaters for recovering struvite (Burns and Moody, 2002; Çelen et al., 2007; Yaffer et al., 2002). Consequently a lot of research has focused on finding the optimum molar ratio of Mg:P for struvite precipitation and the most effective source of magnesium amendment. A number of magnesium sources have been investigated, including magnesium chloride ($MgCl_2.6H_2O$), magnesium oxide (MgO), magnesium hydroxide ($Mg(OH)_2$), and seawater (as it contains high concentrations of Mg).

High purity struvite precipitation is generally observed using Mg:P ratios between 1:1 and 1.3:1 (Adnan et al., 2003; Britton et al., 2005; Fujimoto et al., 1991; Jaffer et al., 2002). It was found that greater phosphorous removal with higher Mg:P ratios is significant because similar phosphorus removal could then be achieved with a little increase in pH. This could result in significant cost savings since it has been estimated that 97% of the chemical costs associated with struvite precipitation are mostly due to the amount of NaOH needed to raise the pH.

Mechanical mixing and seeding

Struvite crystallization progresses from formation of nuclei into complete growth of pellets. The mixing effect enhances the mass transfer of solute to the crystals in the process, resulting in the improvement of struvite crystallization and growth. It has been found that mixing strength and proper seeding materials increase crystal size and improve settleability. Nucleation is controlled by solubility chemistry, while growth rate is believed to be limited by low turbulence or low mixing energy (Ohlinger, 1999). On the other hand, too much turbulence may hinder growth by increasing the collision of individual pellets and thereby breaking the structure, which results in reduced pellet size (Durrant et al., 1999).

A number of studies have investigated the potential of seeding materials to speed up the struvite crystallization reaction. Surface roughness attracts the nuclei embryos and enhances the crystal formation. Generally, struvite pellets or quartz and granite are used as seeding substances. In wastewater streams, because of the absence of seeds in liquids, struvite can preferentially grow on the surface of tanks, pipes and other equipment that act as embryos (Benisch et al., 2002). It was observed that, with respect to phosphorous removal and size distribution of individual pellets, struvite pellets had the best performance among the seeding materials studied. It has also been suggested that seeding is only required at the start-up and the ongoing process eventually becomes self-seeding (Munch and Barr, 2001). Le Corre et al. (2007a) studied the efficiency of a stainless steel mesh system for struvite recovery in a crystallization reactor using synthetic wastewater. They found that the meshes were able to accumulate struvite by capturing crystals already formed in solution, thereby significantly reducing the amount of fine particles left in the solution. Seeding has also been used to produce larger struvite crystals in an effort to make them more acceptable as a direct fertilizer substitute and to enhance recovery of the precipitated crystals.

Presence of other metal ions

Phosphorous generally coprecipitates with available cations, typically calcium, magnesium and ammonium, potassium and ammonium, or potassium and magnesium. Struvite is an ammonium phosphate precipitate with either magnesium or potassium. It has been observed that metals (Ca^{+2}, Al^{+3}) that have greater tendency of precipitating at higher pH could possibly hinder the formation of struvite. These soluble cations provide background competition for the subsequent harvesting of either Mg or Ca phosphates and therefore have the potential to contaminate or diminish the net yield of struvite. Besides, addition of calcium to phosphate solutions will form calcium precipitates (Hydroxyapatite) removing only phosphates in the system, whereas addition of magnesium or potassium provides the opportunity to remove both ammonium and phosphorous. It enables to coprecipitate as "struvite"–magnesium ammonium phosphate or "potassium struvite"–potassium ammonium phosphate.

Due to the increasing demand of nutrient recovery from wastewaters, many technologies are being studied and developed in different parts of the world. These nutrient removal strategies are being viewed as "resource recovery" alternatives for a reliable and sustainable approach in handling excess nutrients at large scale. The following are some of the major technologies that are being operated at full scale facilities around the world.

Nitrogen removal technology

Thermo Energy ARP Technology

Thermo Energy–Ammonia recovery process uses the nutrient rich filtrate obtained from sludge dewatering facilities to recover the high concentrations of ammonia present in it. Ammonia-nitrogen is recovered as ammonium sulfate during this process. Vacuum stripping is done in closed reactors to capture the readily volatilizing ammonia, and then it is

sent through a series of ion-exchange resin adsorption columns. The adsorbed ammonia is regenerated using brine or sulfuric acid and the solutions are stripped of ammonia to produce a commercial-grade (about 40%) solution of ammonium sulfate, which is used as a fertilizer. The first ARP pilot plant was constructed and successfully being operated at Oakwood Beach Water Pollution Control Plant (WPCP) Staten Island, New York.

Phosphorous removal technologies

Phostrip© technology

The Phostrip© Technology recovers phosphorous as calcium phosphate from a phosphorus-enriched sludge processing sidestream. Acetic acid is added to the fermenter to increase the amount of phosphorus released. After the phosphorus-rich water is separated from the sludge, it is treated with lime to precipitate the phosphorus as calcium phosphate. Primary installation of the plant was done in the 1970s in the Reno/Sparks Joint Water Pollution Control Plant located in Sparks, Nevada, U.S. (Levlin and Hultman, 2003) and since then, it is being operated successfully. The Phostrip process is an add-on and does not require significant modification to existing BNR plants.

Crystalactor® technology

The Crystalactor® technology recovers phosphorous as calcium phosphate using sand as the seeding material for crystal development. This process includes addition of lime $Ca(OH)_2$ to the secondary activated sludge, which increases both the pH and the concentration of calcium ions to create optimal conditions for precipitation of calcium phosphate. The Crystalactor® technology has been working in full-scale in The Netherlands, installed at the Geestmertambacht, Heemsted, and Westerbrork (Stack, 2007). The cost of calcium phosphate production used in this process is estimated to be around 22 times higher

than the cost of mined phosphate rock (Roeleved et al., 2004) and thus is not considered viable from a purely economic view.

OSTARA®- Pearl Green process

The Pearl Green process recovers phosphorous as struvite from a nutrient-rich sludge stream with the addition of magnesium chloride. Supplemental caustic soda may be required depending on the alkalinity and hardness of the phosphorous bearing waste stream. A full-scale facility has been in operation at the City of Edmonton, Alberta's Clover Bar sludge processing facility since May 2007. The process uses a fluidized bed reactor to generate the struvite crystals and achieves up to of 80–85% of phosphorous recovery. Additional OSTARA process installations are being installed in Suffolk, VA and Portland, OR (Prasad et al., 2007).

Phosnix process

Another full-scale process is being operated at the Lake Shinji East Clean (LSEC) center in Japan (Ueno and Fujii, 2001) to recover phosphorus as struvite. The process is operated as a fluidized bed reactor, and phosphorus-enriched filtrate from the sludge dewatering process is used as feed. Excess sludge from the plant's biological nutrient removal (BNR) process is digested anaerobically, releasing its phosphorus content. Postdigestion, the phosphorus-rich filtrate is fed with magnesium and sodium hydroxide to adjust the reactor pH and provide an external magnesium source. Recovered struvite is of high purity, which is sold as fertilizer, and the treated effluent with low nutrient concentrations is recycled back to the head works of the plant.

Currently, other emerging technologies for nutrient recovery are KREPO, Seaborne, Aqua-Reci®, Kemicond™, BioCon, SEPHOS, and SUSAN. These technologies focus on

phosphorous recovery from municipal WWTPs and various nutrient-rich streams, recovering it in the form of calcium and iron/aluminum phosphates. It is found that recovery of phosphorous in the form of calcium phosphates can be used as a raw material for phosphorous but iron phosphates cannot be directly used. It requires further treatment to put it into use, which could add up to more operational costs, making it highly uneconomical (Stark, 2005).

Other approaches to recover nutrients have included treating high strength wastewaters from dairy manures, hog or swine manures, beverage industries, leachate, and urine. Human urine is the main nutrient source that contributes about 80% nitrogen (N) and 50% phosphorus (P), but it accounts for less than 1% of the total wastewater volume. If collected and treated, the phosphorus available from urine and feces could account for 22% of the total global phosphorus demand. *No Mix Technology®* by Novaquatis, *Ecosan®-Dry Toilets, Natsol®-Dry Compost Toilets* are some of the current technologies working on nutrient removal from urine. Full scale pilot studies are being operated at Germany, Austria, Netherlands, Sweden, Denmark, Asia (China, Nepal, and Japan) South Africa, France, Australia, the UK, and Luxembourg.

Table 1: Solubility product of Struvite calculated from previous studies.

pK_{sp}	Reference
13.15	Taylor et al., 1963
13.26	Ohlinger et al., 1974
11.84	Booram et al., 1975
9.94	Abbona et al., 1982
13.12	Burns and Finlayson, 1982
12.36	Bhuchanan et al., 1994
12.60	Loewenthal et al., 1994

CHAPTER IV

MATERIALS AND METHODS

Materials

Sludge and mixed liquor samples were collected from local municipal WWTPs in Utah: Central Valley Water Reclamation Facility (CVWRF), North Davis Sewer District (NDSD), South Davis Sewer Distrtict (SDSD) and Snyderville Basin Water Reclamation District (SBWRD). Samples were collected from points in the treatment train where the potential of nutrient availability was high. There are four such sampling points: Primary settled sludge and mixed liquor samples from gravity thickener, anaerobic digestion, and postdigestion processes. Samples were collected in sampling bottles and stored on ice prior to their transport to the laboratory for further analysis. Chemicals used in the experiments are sodium hydroxide-NaOH (Mallinckrodt chemicals), magnesium hydroxide-$Mg(OH)_2$, and magnesium chloride-$MgCl_2.6H_2O$ (Fisher Scientific) of pure laboratory grade.

Experimental setup

A series of bench top experiments were performed on fifty milliliters of supernatants obtained from mixed liquor and sludge samples in order to study the influence of supernatant composition and the presence of metal ion concentrations on struvite precipitation. Nutrient recovery was accomplished by addition of different chemicals under a controlled pH range of 8–10. Fifty milliliters of working volume was maintained for all the experiments. Ten milliliters of the sample was filtered separately and used to measure the

concentration of magnesium and other metals present in the solution using inductively coupled plasma mass spectrometry (ICP-MS) analysis as struvite precipitation is mainly inhibited by the presence of other metal ions. For each experiment condition, fifty milliliters of supernatant of sample was taken in a beaker and placed on a magnetic stir plate. The chemicals were added in the form of solution from their standard stock solutions, ensuring complete mixing of the chemicals. pH of the samples was controlled and monitored between 8–10 to not to exceed the solubility limit. After the addition of chemicals, samples were subjected to a mixing speed of 180 rpm on the magnetic stir plate. A mixing time of 25–30 minutes was given, and then the samples were allowed to settle down in conical tubes. Conical tubes were used to enhance the settling of the precipitate formed. After settling, supernatants of each sample were collected, filtered, and analyzed for ammonia-nitrogen and orthophosphate concentrations in the solutions.

Of the three main constituents in struvite, orthophosphate (PO_4-P) is the limiting parameter in digestion and postdigestion processes, which determines the amount of struvite that can possibly be formed on a molar basis. Within the favorable pH range of struvite crystallization i.e. 7–10, concentrations of total orthophosphorous (PO_4^{3-}) in the solution has a greater influence on struvite precipitation than does the pH effect on NH_4^+ activity (Stumm and Morgan, 1970). Stoichiometric ratios of NH_4:Mg^{+2}:P within the range of 1:1:1 to 1:1:1.3 have been reported for maximum nutrient recovery (Jaffer et al., 2003; Ohlinger et al., 1998). Therefore, from the baseline concentration of metals from ICP-MS analysis, the initial concentration of Mg^{+2} was taken, and accordingly the external magnesium source stock was made to have an optimum ratio of 1:1:1.2 or 1.3 (NH_4:Mg^{+2}:P) in the final solution. All the reactors had received equimolar ratios of the three constituents to achieve maximum recovery. Samples were processed immediately after collecting them, avoiding

volatilization of ammonia. All the samples had pH around 6.9–7.2, which would not cause ammonia to volatilize. Volatilization of ammonia nitrogen increases around pH 9. For one set of samples, operational parameters pH and temperature were studied under the addition of NaOH and $MgCl_2$. For these experiments, a stoichiometric ratio of Mg source was added and accordingly the pH and temperature were varied to study their effect on struvite precipitation. For the other set of samples, struvite was precipitated using three different chemicals, sodium hydroxide (NaOH), magnesium hydroxide ($Mg(OH)_2$), and magnesium chloride ($MgCl_2$), to analyze the maximum recovery that can be achieved by varying the chemicals under controlled pH. Sodium Hydroxide simulated the increase of pH of samples. Addition of $MgCl_2$ and $Mg(OH)_2$ chemicals served the purpose as external Mg^{+2} sources. Concentrations of samples were measured before and after the addition of chemicals. The advantage of using $MgCl_2$ is that it dissociates faster, resulting in shorter reaction times. From the concentrations (C) of ions before and after precipitation, the percentage removal of nutrients was calculated as follows:

$$\%\text{Removal} = \left(\frac{C_{\text{before adding chemicals}} - C_{\text{after addingchemicals}}}{C_{\text{before adding chemicals}}}\right) * 100 \qquad (14)$$

Analytical methods

Mixed liquor and sludge samples collected from the treatment plants were centrifuged (Beckman Coulter®-Allegra 64R) for ten minutes at a speed of 6500rpm to get rid of the suspended content and supernatants were collected. Supernatants were filtered with 0.45μm (Fisher Scientific®) filter paper and analyzed for various nutrient parameters. pH of the samples were measured using a HACH® pH/ORP probe. Ammonia-nitrogen (NH_3-N) was measured using HACH® methods 10031 (Salicylate method), and optical

densities of the samples were measured at a wavelength of 655 nm (HACH®DR5000 spectrometer). Phosphorous (PO_4-P) was measured in ion chromatography (IC-Metrohm® 883 Basic IC plus). Metal ions present in the solution were analyzed using ICP-MS analysis.

CHAPTER V

RESULTS AND DISCUSSIONS

Central Valley Water Reclamation Facility (CVWRF)

Central Valley is the largest wastewater facility in the state. It is designed for a maximum flow of 75 million gallons per day (MGD) and currently receives an average annual influent flow of 49 MGD. Central Valley uses a trickling filter solids contact (TF/SC) process as their biological treatment. Anaerobic egg-shaped digesters treat the solids, which are later applied to land as class A compost (33%) and class B biosolids (67%). The treated water is cleaned and released to the Millcreek/Jordan River system.

Mixed liquor samples having high nutrient concentrations in the treatment train were collected throughout the year at different times (spring and summer). Samples were collected from filtrate, supernatant from anaerobic digester, and secondary settled sludge and primary settled sludge from the treatment chain. Compositions of liquors from TF/SC process are 30–70 mg P/L, 1000–1300 mg NH_4-N mg/L as a consequence of anaerobic digestion of waste sludge. Baseline concentrations of nutrients and metal ions present in the samples are summarized in Table 2 (spring) and Table 3 (summer) for different sampling events. The characteristics of the sludge vary depending upon the origin of sludge, time of the year when it had been collected, and the type of process that it has been subjected to (Metcalf and Eddy, 1979). From Tables 2 and 3, it is evident that the concentrations of metals and nutrients have been lower in the summer than in spring, which could be attributed to the

increased springtime inflow to the plant as a result of snowmelt and runoff to the plant influent.

In most of the samples, concentration of metals such as magnesium, calcium and potassium were observed to be higher than the concentrations of orthophosphate in the solution. However, in the filtrate samples the concentration of magnesium was found to be lower than phosphorous, calcium, and potassium. This could be due to the alkalinity present or due to the release of intracellular substances from the microbial cells in the mixed liquors during anaerobic digestion. Low phosphorous concentrations in the plant could be due to the low incoming phosphorous to the plant or due to the TF/SC, operating as the biological unit. Microorganisms thrive on the nutrients to break down the organics and thus could cause in low phosphorous concentration. A portion of it would be released back during the anaerobic digestion, which will be recirculated back to the headworks. Nutrient recovery tests were conducted at different operational conditions to evaluate the effect of pH and temperature on struvite precipitation. NaOH was added to increase the pH of the solutions, and $MgCl_2$ was added as a source of Mg for the experiment. Based on the ICP-MS analysis, the external source of magnesium was supplied to the samples so as to have the optimum ratio of NH4:Mg:P in 1:1:1.2 or 1.3 in the final solution to achieve maximum recovery.

Figures 1 and 2 show the percentage of phosphorous and nitrogen removal in the samples (collected during spring) at different pH values as a result of struvite precipitation and other mineral precipitation (i.e, calcium phosphate) due to the addition of NaOH and $MgCl_2$. From Table 3 we can see that although the removal of ammonia and phosphorus at all pH values was recorded, the maximum removal efficiencies were recorded at the pH range of 8.5–9 with phosphorous removal efficiency as high as 90.1%, and the ammonia removal efficiency was 27.7%. Low ammonia removal efficiency was possibly due to the fact

that not much phosphorous was available for ammonia to combine and form precipitates such as struvite. Hence, it can be concluded that both magnesium and phosphorous are limiting constituents in the samples for struvite precipitation. However, if we look at the baseline concentrations for ammonia and phosphorus for primary and secondary sludge, these samples contained phosphorous concentrations such that, almost 70–80% of ammonia concentrations are present in these samples, and yet both ammonia and phosphorus removal efficiencies in these two samples never crossed 30% at an optimum pH of 8.5–9, whereas phosphorous removal of same samples at the optimum pH was as high as 73.7%. This implies that other mechanisms other than just struvite precipitation were also contributing to phosphorous removal from the solution.

To evaluate the effect of temperature on struvite precipitation, optimum pH was used. Based on the optimum pH obtained from the above experiments, the pH was maintained at 8.5–9 and the temperature was varied from t–4, 28, 37, 42^{o}C. To maintain the temperature throughout the experiments, tests were conducted inside the incubators. All the solutions were provided with NaOH and $MgCl_2$ to facilitate the optimum conditions for struvite precipitation. Based on the data, it can be seen that as the temperature increased, nutrient removal in the solution has also increased until 28^{o}C and then it tends to decrease. Figures 3 and 4 show the percentage removal of nitrogen and phosphorous in the samples at different temperatures (maintained at optimum pH). It can be concluded that the temperature value of 28^{o}C was optimum for ammonia and phosphorus removals. Also, in general, the removal was relatively lower at 4^{o}C**.** Table 4 represents nutrient removal achieved from struvite precipitation experiments by adding NaOH and $MgCl_2$ at pH 8.5–9 and at different temperatures. Samples were collected in summer as well to see the seasonal changes in the nutrient recovery tests. From Table 2, it is evident that the concentration of

nutrients and metals has decreased by more than 50%, which could be because of the increased activity of microorganisms during the treatment process. The same protocol was repeated for the nutrient recovery experiment. Magnesium stock concentration was calculated from ICP-MS analysis values. For nutrient recovery tests conducted under different pH, a similar trend was observed. Samples have shown maximum recovery in the pH range of 8.5–9, with percentage of phosphorous and nitrogen removal to be around 90% and 24%, respectively.

Since magnesium and phosphorous are limiting constituents, in order to achieve complete removal of nutrients it is suggested that both phosphorous and magnesium have to be added externally. Figures 5 and 6 show the percentage of phosphorous and nitrogen removal in the samples (collected during summer) at different pH values as a result of struvite precipitation or other mineral precipitation (i.e, calcium phosphate) due to the addition of NaOH and $MgCl_2$. Variation of temperatures in the nutrient recovery test also showed the same trend. Nutrient recovery increased until 28^{o}C and then decreased. Figures 7 and 8 shows the percentage removal of nitrogen and phosphorous in the samples at different temperatures (maintained at optimum pH). From a previous study, according to Bhuiyan et al. (2007), solubility of struvite increases with increasing temperature until it reaches the maximum solubility at 35^{o}C and then declined. Percentages of nutrient removal achieved from different operating conditions are shown elaborately in the appendix with their corresponding base concentrations. We can say that, extreme high or low temperatures do not favor nutrient recovery in the samples. Although all the samples have the potential to recover, favorable conditions for each sample have to be optimized based on the incoming nutrient stream.

North Davis Sewer District (NDSD)

NDSD treatment plant was designed for maximum monthly flow of 41 MGD and currently receives an average annual influent flow of 21 MGD. Wastewater is treated with ferric chloride at the primary treatment and then sent to the trickling filters. The facility operates a TF/SC process as a biological unit followed by secondary sedimentation. Residual primary and secondary solids are thickened and stabilized using conventional mesophilic anaerobic digestion, mechanically dewatered (using belt presses), and composted. Samples were collected from filtrate, supernatant from anaerobic digester, and secondary settled sludge and primary settled sludge from the treatment chain, which had high nutrient concentrations. All the samples were characterized and tested for nutrient recovery tests.

Baseline concentrations of nutrients and metal ions present in the samples are summarized in Tables 4 and 5 for different sampling events. From the tables, we can see that concentrations of nutrients and metals have almost been the same during different sampling events. Strength of incoming sewage fluctuations were very little leading to negligible change in nutrients and metals present in it. High amounts of iron have been observed in the primary sludge, which could be attributed to the addition of ferric chloride to achieve better solids removal in the system. High concentrations of sodium and calcium were observed during the fall, which could be due to the high alkalinity present in wastewaters. Nutrient recovery was studied by using three different chemicals: sodium hydroxide (NaOH), magnesium hydroxide ($Mg(OH)_2$), and magnesium Chloride ($MgCl_2$). Sodium hydroxide caused an increase of the pH in the samples to optimum pH, without the addition of external Mg^{+2} salts. $MgCl_2$ addition simulated a condition in which external Mg^{+2} were added. The addition of $Mg(OH)_2$ raised the pH as well as added Mg^{+2} salt externally. The advantage of using $MgCl_2$ is that it dissociates faster than $Mg(OH)_2$, resulting in shorter reaction times.

However, magnesium Hydroxide ($Mg(OH)_2$) is generally cheaper but is highly insoluble and takes longer time to dissolve into the solution.

In all the experiments phosphorous was the limiting substance for struvite precipitation stoichiometrically. Magnesium sources were added accordingly to favor the precipitation reaction with a ratio being maintained at Mg:P of 1.3:1. From the experiments it was observed that by the addition of sodium hydroxide to the mixed liquor samples, reduction in phosphate (PO_4-P) concentrations were observed to be 75–80% during both the sampling events. From this it can be inferred that only by raising the pH itself, about 85% of nutrient recovery of phosphorous can be achieved in all the samples. A white cloudy precipitate was observed at the bottom of the conical tubes where the samples were allowed to settle after struvite precipitation. By adding $Mg(OH)_2$, it was found that the nutrient recovery (in terms of phosphate concentrations) is around 65–70%. Initially, the gravity thickener showed no decrease in phosphate concentration, which can be because of limiting orthophosphate content in the mixed liquor samples (not sufficient enough to form struvite or could have interfered with other probable metal ions) but later experiments showed that supernatant from the gravity thickener though small, had the potential of recovering nutrients.

Upon addition of $MgCl_2$, samples have shown maximum reduction in orthophosphate and ammonia-nitrogen levels, which can be attributed to the increased Mg:P ratio as ($MgCl_2$) acts as a source of magnesium, but does not increase the pH. Adding NaOH along with $MgCl_2$ simultaneously is considered to be beneficial as NaOH will increase the pH, and $MgCl_2$ can be used to maintain the ratio of Mg:P simultaneously. For samples collected during the fall, it was not the same. Samples showed less efficiency in precipitating struvite. Even though $MgCl_2$ provides a higher Mg:P ratio, the low P concentration resulted

in inefficient nutrient recovery. There could also be experimental error. Nitrogen removal was around 20–25% at the three conditions due to limited phosphorous present to form struvite and almost followed the same trend throughout the sampling events. Figures 9, 10, 11, and 12, respectively show percentage removal of nutrients (ammonia-nitrogen and phosphorous) observed in struvite precipitation with the addition of different chemicals for different sampling events. The percentages of nutrient removals achieved from different operating conditions in the experiments are shown elaborately in the Appendix with respect to their base concentrations.

Among all the samples, high nutrient recovery rates were observed in samples from filtrate and digesters, which had high ammonia and phosphorous concentrations. There can be other metal ions that have been precipitated with phosphorous, most likely calcium and potassium precipitates, interfering with the struvite precipitation. Mustovo et al. (2000) suggested that Mg:Ca should exceed 3:5 to achieve struvite formation in preference to Ca-phosphates. From this we can say that though there could be some interference or precipitation with suspended particles in the solution, the recovered product could be mostly struvite in the samples. Further analysis of the precipitate formed by x-ray diffraction studies can give us more details into the chemistry of the precipitate formed.

South Davis Sewer District (SDSD)

North plant

The north plant is designed for an average flow of 12 MGD and currently treats an average annual flow of approximately 8 MGD. The present treatment facility operates a single-stage trickling filter process as the biological unit with primary treatment and secondary sedimentation followed by chlorination and dechlorination processes to meet their effluent limits. Effluent is re-oxygenated (to maintain the DO content) before it is

discharged to the receiving waters. Tricking filter solids are cosettled with primary solids in the primary clarifier, thickened with secondary solids, and stabilized using conventional mesophilic anaerobic digestion. Digested solids are air dried in sludge drying beds, and the biosolids are beneficially used for land applications. Centrate obtained from the sludge drying beds (collected at the bottom of the beds by the action of gravity) is recycled back to the beginning of the plant as a slug load. Primary treatment involves a conventional approach (i.e., addition of alum at a controlled rate to achieve maximum separation of solids and liquids at the primary clarifier).

Samples were collected from different parts of the treatment train having high nutrient concentrations. All the samples were characterized for basic parameters and tested for nutrient recovery by adding three different chemicals to see which chemical favored high nutrient recovery, and the conditions were optimized for maximum recovery. Baseline concentrations of nutrients and metal ions present in the samples are summarized in Tables 6 and 7 for different sampling events at the north plant of SDSD. From the tables, we can see that both the sampling events had relatively similar concentrations of metals coming into the plant, with the only change occurring in the observed nutrient concentrations. Samples collected during spring had high nutrients, which could be due to the high strength waters coming from the surrounding industries or due to excess fertilizer applications in the county. On the day when samples were collected, the secondary clarifier of the plant was being cleaned and as a result, the wastewater flow at certain parts in the treatment process was being regulated accordingly and causing more change in nutrient concentrations at the plant than usual.

Nutrient recovery was tested by adding different chemical to samples. pH was raised using NaOH, and the magnesium source was provided with $MgCl_2$ and $Mg(OH)_2$. The same

nutrient recovery protocol has been followed. During the experiments, no visible precipitate has formed, particles were observed to stick on the walls of the conical tubes, but when the concentrations of nutrients are measured before and after the addition of chemicals, a significant decrease has been observed. Struvite precipitation is formed when the concentration of ions exceeds its Solubility limit; otherwise will be dissolved. Figure 13 represents the percentage of phosphorous removal observed by addition of different chemicals for samples collected at north plant during spring.

For samples collected in spring from the primary clarifier and thickener, addition of NaOH caused phosphate concentration to go down by approximately 85 and 65%, respectively, even if these samples did not have any ammonia to start with. This is because of phosphate precipitation with other metal ions to form metal phosphates rather than struvite. For samples collected from the digester and drying bed, struvite precipitation caused both ammonia and phosphorus removals to be around 23% and 87%, respectively. Addition of $Mg(OH)_2$ caused higher removal of nutrients in the samples due to the increased Mg:P ratio as ($Mg(OH)_2$) acts as a source of magnesium, but dissociation of $Mg(OH)_2$ takes a longer time, increasing reaction times. Excess magnesium in the sample can also increase the background competition for calcium to precipitate with phosphorous. Addition of $MgCl_2$ caused around 50% phosphorous removal and nitrogen removal was less than 25% in all the samples.

For samples collected in the summer, nutrient recovery was achieved with a higher percentage of removal, due to the presence of significant nutrient concentrations in the samples. Raising the pH to 8.8 by adding NaOH only caused around 83% recovery of phosphorous and 24% of nitrogen removal in the digester and sludge drying bed samples. Gravity thickener samples also showed potential of nutrient recovery unlike previous

sampling. $MgCl_2$ recovered a higher percentage of nutrients than $Mg(OH)_2$ around a pH >8.5 due to immediate dissociation of the $MgCl_2$ ions, favoring greater struvite precipitation. Precipitates were observed to be formed at the bottom of the conical tubes. Figures 14 and 15 represent the percentage of nitrogen and phosphorous removal observed by addition of different chemicals in summer. The percentages of nutrient removal achieved from different operating conditions are shown elaborately in the Appendix with their base concentrations.

South plant

The south plant is a relatively small plant receiving 4 MGD of water daily. It receives waters from the surrounding industries and oil refineries and operates similar to the north plant. The plant is mainly regulated for total nitrogen content in the effluents. Effluent from the plant is discharged into the Jordan River. Chlorine and sulfur dioxide are used for the disinfection process before discharge of effluents. Solids are stabilized using mesophilic digestion. The reduced solids are air dried and used for land application purposes. Samples were collected from different locations in the treatment plant. Nutrient recovery tests have been performed at two different times of the year in the south plant, and significant recovery of nutrients has been observed from the samples. The south plant receives similar concentrations of nutrients and metals as the north plant, except high concentrations of sodium and potassium have been observed in the samples. This could be due to the excess use of sodium/potassium salts at the industries. Nutrient recovery tests have shown consistent results and a similar trend in all the samples, which makes it a direct solution for struvite recovery if it were to be applied real time at the plant.

All the samples were characterized for basic parameters, tested for nutrient recovery by adding three different chemicals to see which chemical favored high nutrient recovery and the conditions were optimized for maximum recovery. From the results of the nutrient

recovery tests it has been observed that the addition of NaOH alone had caused a significant amount of recovery forming white cloudy precipitate at the bottom of the conical tubes. Both $Mg(OH)_2$ and $MgCl_2$ showed a high percentage of phosphorous recovered, with $MgCl_2$ causing maximum recovery at a pH around 9. With high concentrations of potassium and calcium present, when compared to magnesium, the recovered product could not exactly be determined as struvite. Adding NaOH along with $MgCl_2$ simultaneously is considered to be more beneficial as NaOH will increase the pH, and $MgCl_2$ can be used to maintain the ratio of Mg:P simultaneously. Further analysis of the precipitate formed by x-ray diffraction studies can give us more details into the chemistry of the precipitate formed. The baseline concentration of nutrients and metal ions and their corresponding nutrient removal results have been shown in the following tables. Tables 8 and 9 represent the baseline concentrations of metals and nutrients present in the samples (collected during fall and spring respectively). Figures 16, 17 and 18 represents the percentage of phosphorous and nitrogen removal observed by addition of different chemicals in spring and summer for the South Davis sewer district–south plant. Percentage of nutrient removals achieved from different operating conditions is shown elaborately in the Appendix with respect to their base concentrations.

Snyderville Basin Water Reclamation District (SBWRD)

Snyderville basin-East Canyon water reclamation (SBWRD) facility is the only plant in the state operating a full-scale enhanced biological phosphorous removal plant (EBPR). It is designed to treat a capacity of 4 MGD from Park City, the Canyons, and the western Snyderville Basin and returns the cleaned water to East Canyon Creek, which then flows into the East Canyon Reservoir. The plant treats incoming water by mechanical screening followed by activated carbon beds (to reduce odor levels). Mixed liquor is then sent to the

anaerobic, anoxic, and oxic bioreactor for the EBPR process to take place, followed by chemical treatment, sand filtration, and UV disinfection to remove trace amounts of phosphorous and other organics. Effluent concentration of <0.1 mg/l of TP is achieved through the treatment. Solids are landfilled after they are dewatered in the centrifuge and the filtrate is recycled back to the headworks. Sampling was done only once and the samples were collected from secondary clarifiers and filtrate of the plant. Samples were characterized for basic parameters and nutrient recovery was accomplished by addition of three different chemicals, and the conditions were optimized for maximum recovery of nutrients.

Baseline concentrations of nutrients and metal ions present in the samples are summarized in Table 10. From the table we see that the ammonia-nitrogen concentrations are lower when compared to the phosphorous concentrations, clearly due to the phosphorous removal treatment that the plant exhibits. All the phosphorous content is concentrated in the solids, producing phosphorous-rich sludge, and some of it is released due to the dewatering process. If the EBPR process were integrated with anaerobic digestion, then high amounts of ammonia nitrogen would have been observed in the filtrate along with phosphorous. Since ammonia is also the limiting agent, ammonium chloride was added to all the samples to increase the final ammonium concentration. Nutrient recovery protocol was followed, and the samples were treated for different conditions. Addition of NaOH reduced the concentrations of nutrients significantly, with a recovery percentage up to 70%. Though significant amounts of ammonia and phosphorous were present, magnesium was insufficient, and there would have been other metal ions coprecipitating with struvite that led to the reduction of the nutrient concentrations. By adding Mg as an external source, the phosphorous recovery was observed to be around 95% and even the nitrogen reduction was found to be around 92%. Figures 19 and 20 show the percentage

removal of nutrients achieved through struvite precipitation. White colored precipitate was clearly visible in the conical tubes. Both $MgCl_2$ and $Mg(OH)_2$ had shown relatively similar removal potentials, but $Mg(OH)_2$ has higher reaction times making it undesirable ($MgCl_2$ being slightly more efficient).

Samples from the East Canyon plant had nutrient recovery potential. If the EBPR plant had used anaerobic digestion to treat its solids, then it could substantially recover a high percentage of nutrients from the filtrate as anaerobic digestion releases high ammonium and phosphorous concentrations. For maximum nutrient recovery in the form of struvite to occur, equimolar concentrations of constituent ions have to be present under favorable pH conditions. The percentage of nutrient removals achieved from different operating conditions is shown elaborately in the Appendix with respect to their base concentrations.

Table 2: Baseline concentrations of nutrients and specific metal ions present in CVWRF samples (collected in spring)

	Na mg/l	Mg mg/l	Al mg/l	Ca mg/l	K mg/l	Fe mg/l	NH_3-N mg/l	PO_4-P mg/l
Primary sludge	514	119	1.1	456	91	23	65	40
Secondary sludge	299	61	2.1	184	44	<4.6	52	36
Anaerobic digester	267	57	2.1	223	165	<4.6	784	46
Filtrate	207	35	9.1	197	143	<4.6	894	68

Table 3: Baseline concentrations of nutrients and specific metal ions present in CVWRF samples (collected in summer)

	Na mg/l	Mg mg/l	Al mg/l	Ca mg/l	K mg/l	Fe mg/l	NH_3-N mg/l	PO_4-P mg/l
Primary sludge	166	60	0.2	291	32	10	58	45
Secondary sludge	141	33	0.1	76	19	0.4	55	33
Anaerobic digester	204	12	0.2	116	140	1.4	857	53
Filtrate	174	8	0.1	95	121	0.7	1304	63

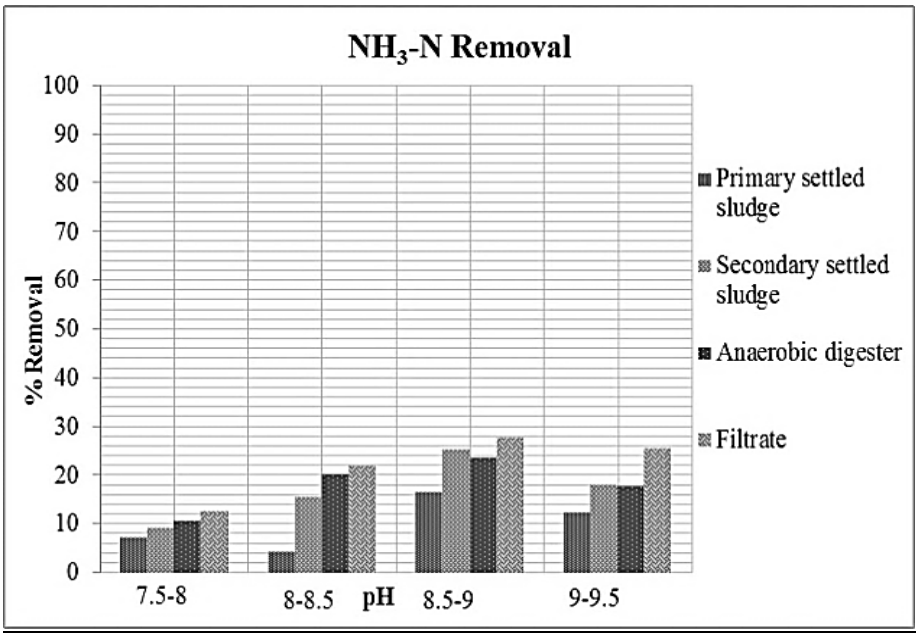

Figure 1: Percentage of nitrogen removal observed in CVWRF samples at different pH (collected during spring)

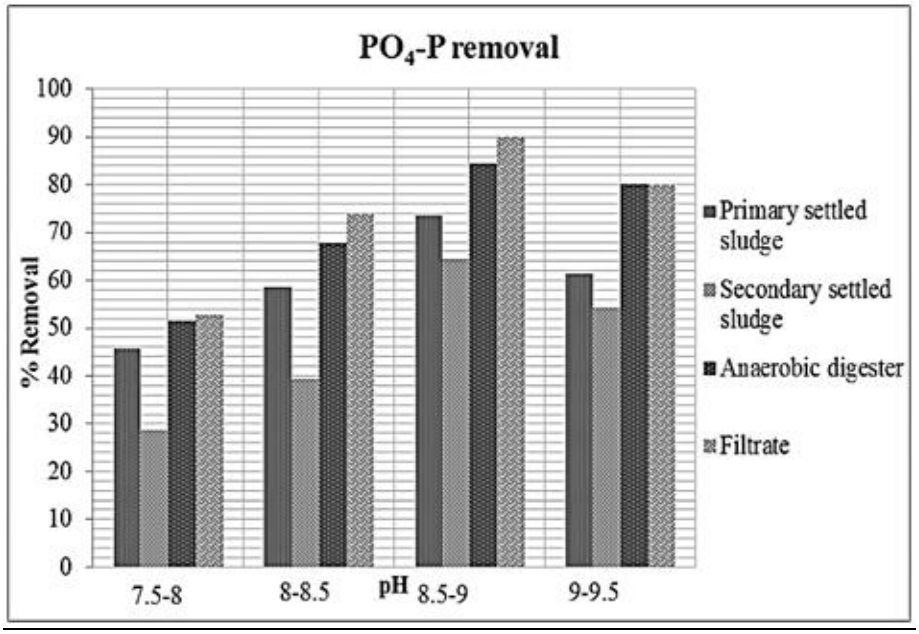

Figure 2: Percentage of phosphorous removal observed in CVWRF samples at different pH (collected during spring)

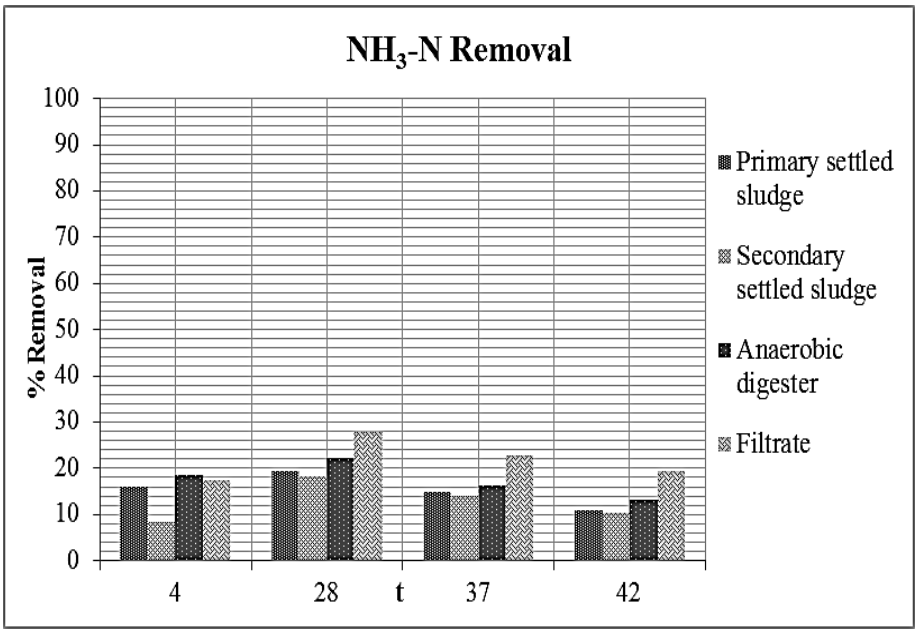

Figure 3: Percentage of nitrogen removal observed in CVWRF samples at different temperatures and a pH of 8.5 to 9 (collected during spring).

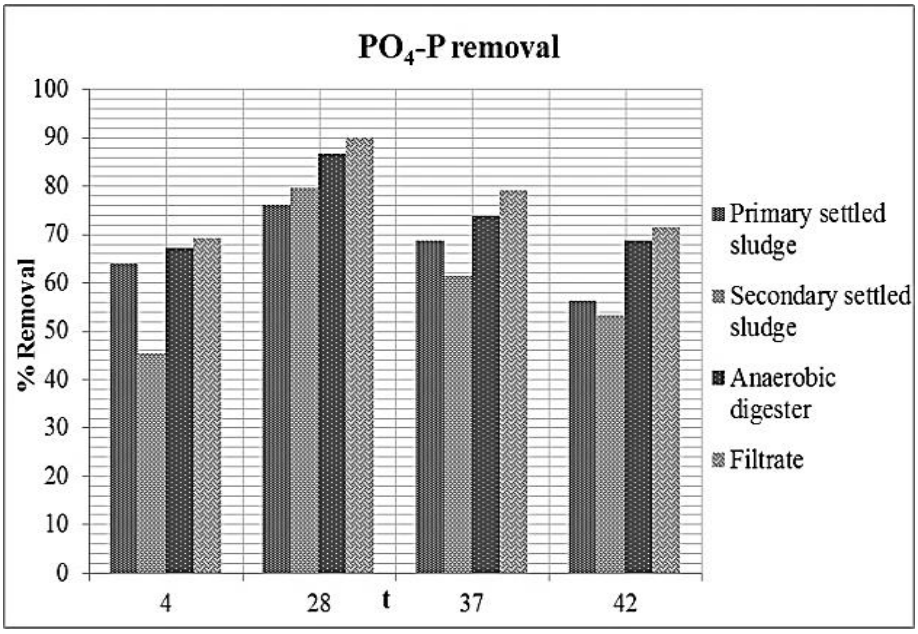

Figure 4: Percentage of phosphorous removal observed in CVWRF samples at different temperatures and a pH of 8.5 to 9 (collected during spring)

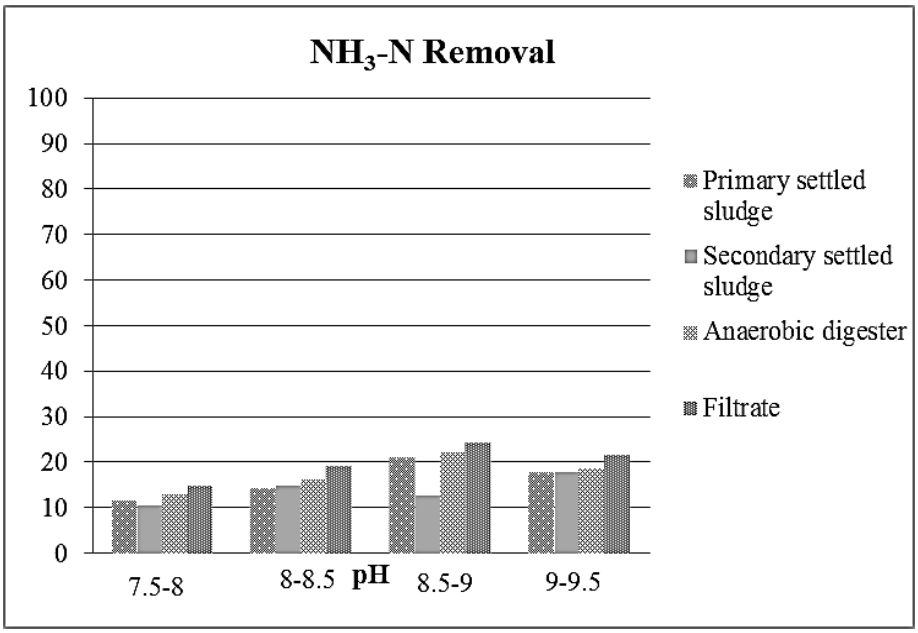

Figure 5: Percentage of nitrogen removal observed in CVWRF samples at different pH (collected during summer)

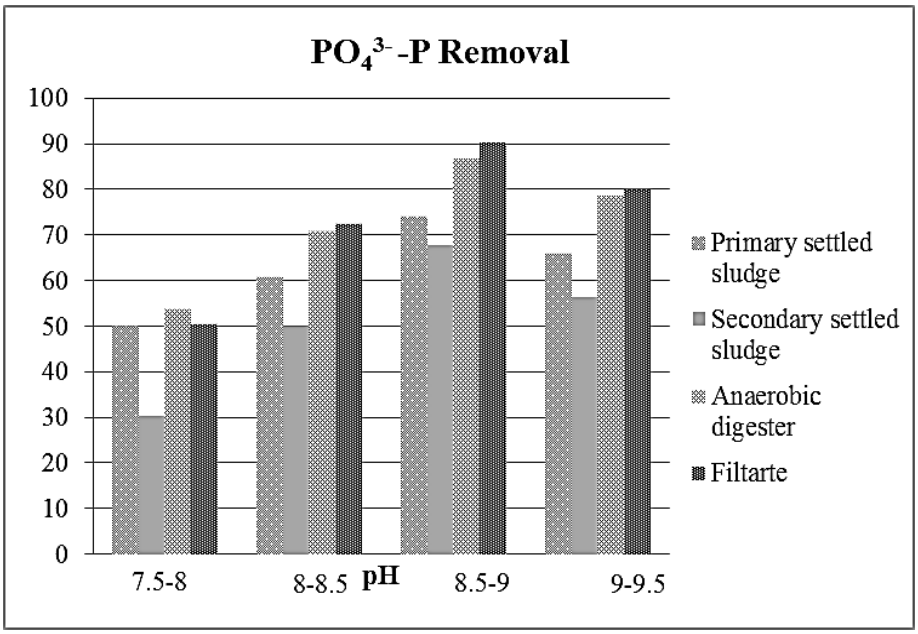

Figure 6: Percentage of phosphorous removal observed in CVWRF samples at different pH (collected during summer)

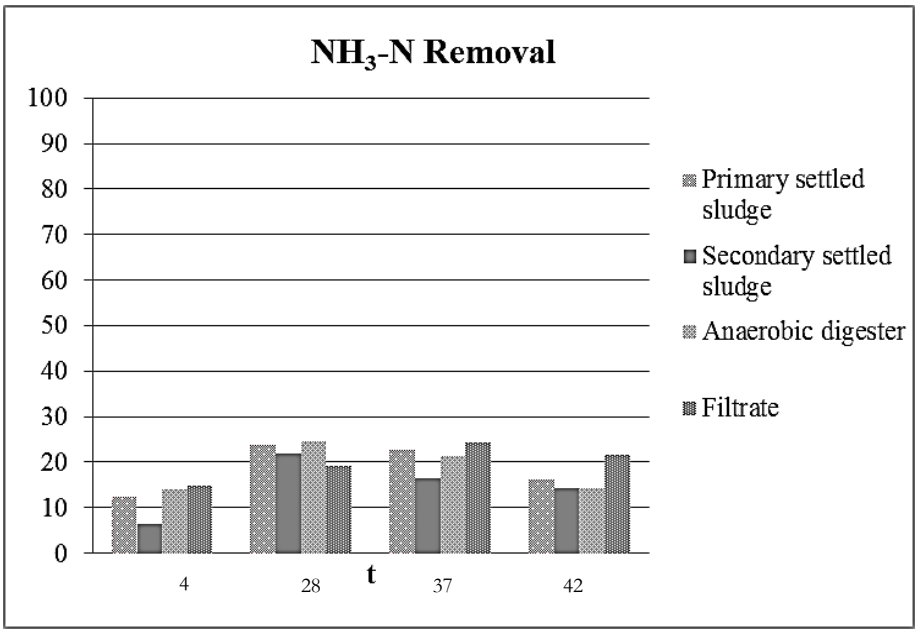

Figure 7: Percentage of nitrogen removal observed in CVWRF samples at different temperatures and a pH of 8.5 to 9 (collected during summer).

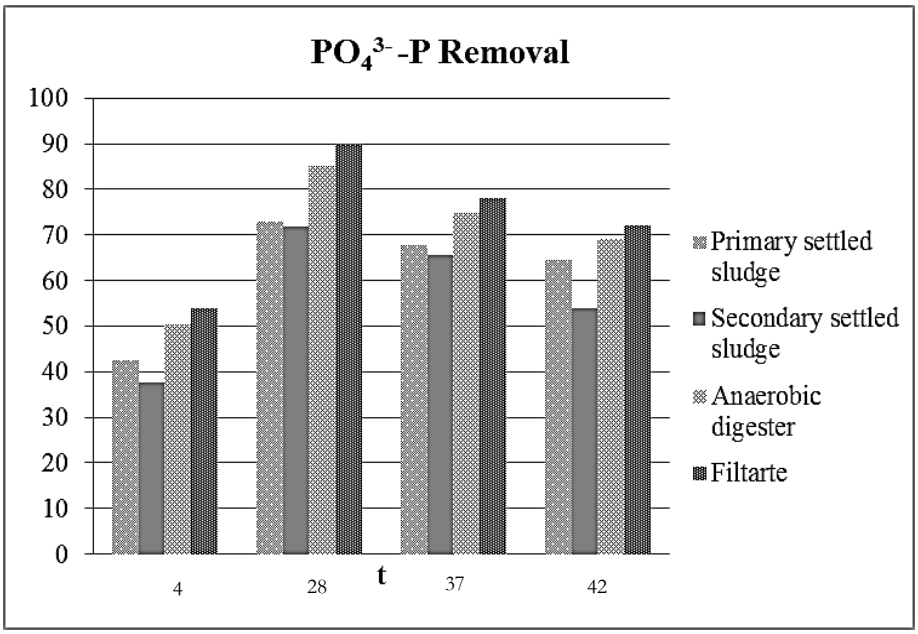

Figure 8: Percentage of phosphorous removal observed in CVWRF samples at different temperatures and a pH of 8.5 to 9 (collected during summer).

Table 4: Baseline concentrations of nutrients and specific metal ions present in NDSD samples (collected in fall)

	Na mg/l	**Mg mg/l**	**Al mg/l**	**Ca mg/l**	**K mg/l**	**Fe mg/l**	**NH_3-N mg/l**	**PO_4-P mg/l**
Primary sludge	283	119	0.8	437	40	59	45	16
Gravity Thickener	126	29	0.5	57	24	<0.1	39	10
Anaerobic digester	161	52	12	88	100	3	730	24
Filtrate	148	38	0.4	64	90	<0.1	754	27

Table 5: Baseline concentrations of nutrients and specific metal ions present in NDSD samples (collected in summer)

	Na mg/l	**Mg mg/l**	**Al mg/l**	**Ca mg/l**	**K mg/l**	**Fe mg/l**	**NH_3-N mg/l**	**PO_4-P mg/l**
Primary sludge	196	66	0	149	49	18	42	29
Gravity Thickener	167	36	0	68	20	<0.2	34	15
Anaerobic digester	206	64	0.1	96	109	0.4	744	26
Filtrate	180	52	0.1	73	82	<0.2	773	33

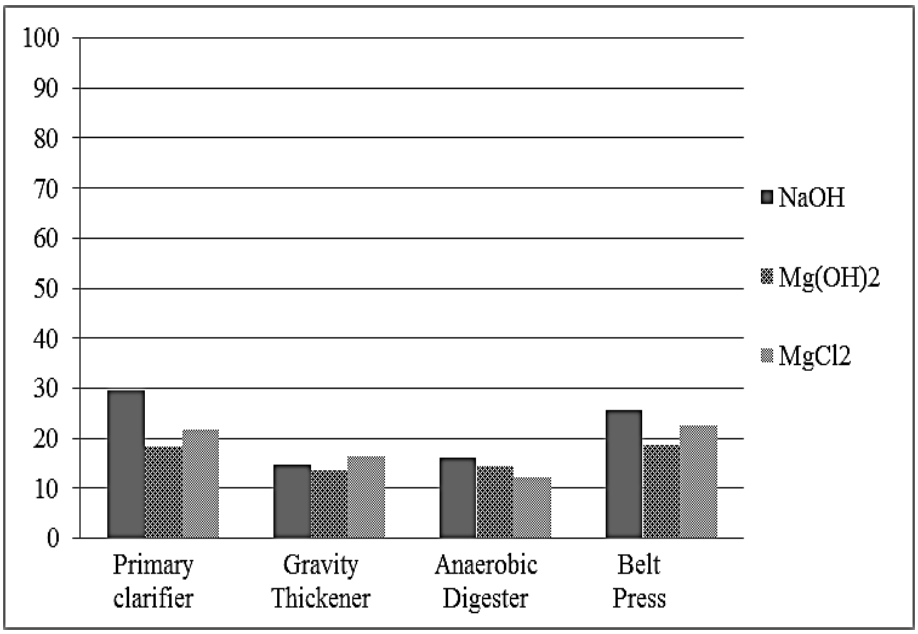

Figure 9: Percentage of nitrogen removal observed in NDSD samples due to addition of different chemicals (collected during fall).

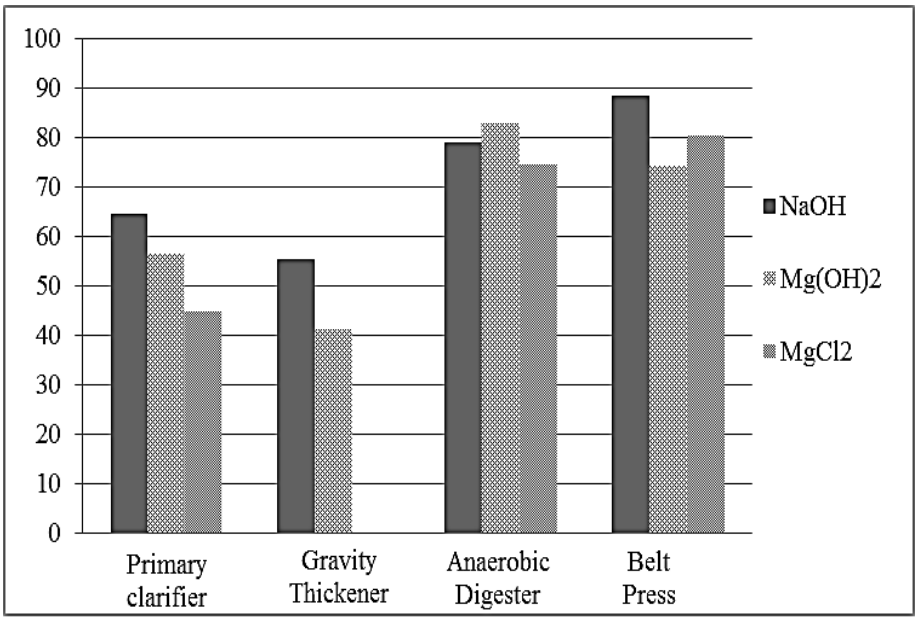

Figure 10: Percentage of phosphorous removal observed in NDSD samples due to addition of different chemicals (collected during fall).

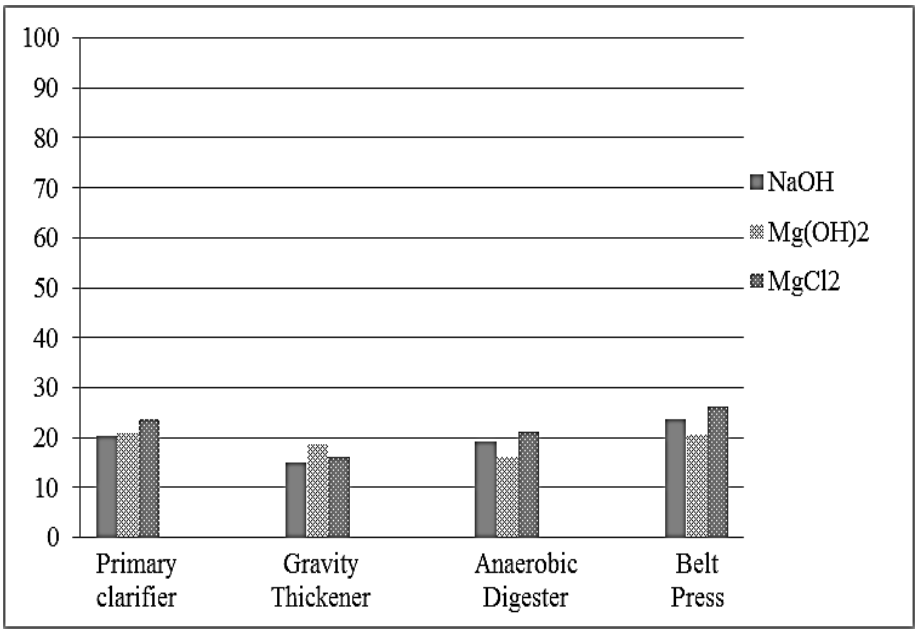

Figure 11: Percentage of nitrogen removal observed in NDSD samples due to addition of different chemicals (collected during summer).

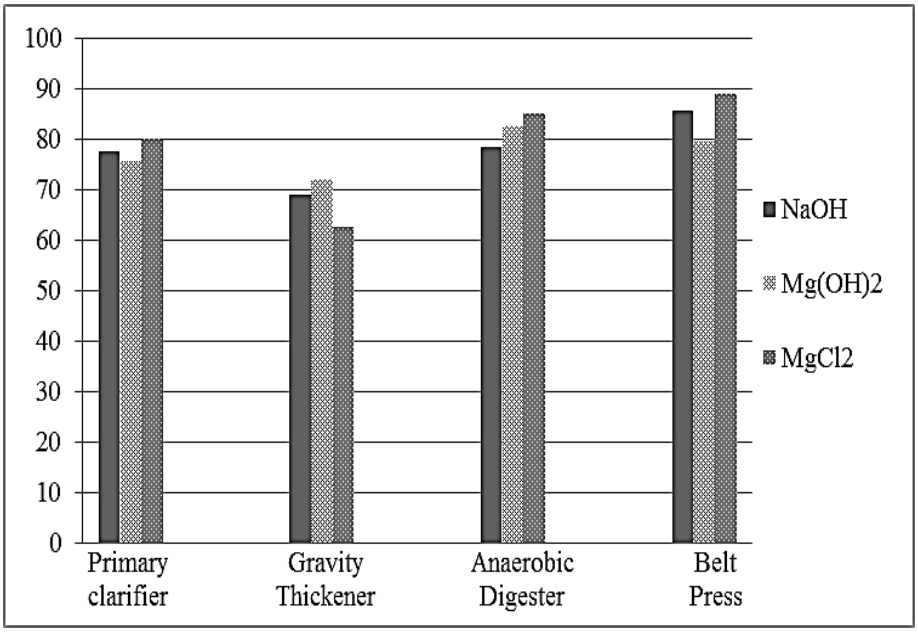

Figure 12: Percentage of nitrogen removal observed in NDSD samples due to addition of different chemicals (collected during summer).

Table 6: Baseline concentrations of nutrients and specific metal ions present in SDSD-north plant samples (collected in spring).

	Na mg/l	**Mg mg/l**	**Al mg/l**	**Ca mg/l**	**K mg/l**	**Fe mg/l**	**NH_3-N mg/l**	**PO_4-P mg/l**
Primary sludge	220	35	1.8	101	27	0.7	-	16
Gravity Thickener	244	40	1.4	119	27	<0.2	-	7
Anaerobic digester	256	57	1.4	122	90	1.2	658	89
Sludge drying beds	378	72	0.9	141	123	1.3	733	67

Table 7: Baseline concentrations of nutrients and specific metal ions present in SDSD-north plant samples (collected in spring).

	Na mg/l	**Mg mg/l**	**Al mg/l**	**Ca mg/l**	**K mg/l**	**Fe mg/l**	**NH_3-N mg/l**	**PO_4-P mg/l**
Primary sludge	262	55	<0.03	149	55	8.4	53	17
Gravity Thickener	246	37	0.5	98	27	0.7	30	11
Anaerobic digester	270	65	0.1	132	101	3.9	831	29
Sludge drying beds	404	48	0.1	114	162	0.6	869	34

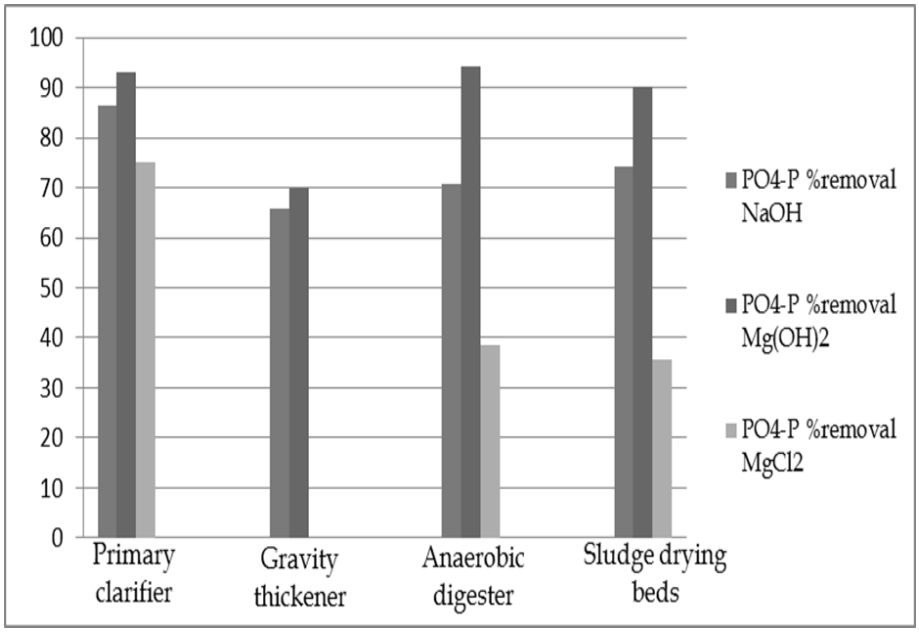

Figure 13: Percentage of phosphorous removal observed in SDSD samples due to addition of different chemicals in north plant (collected during spring).

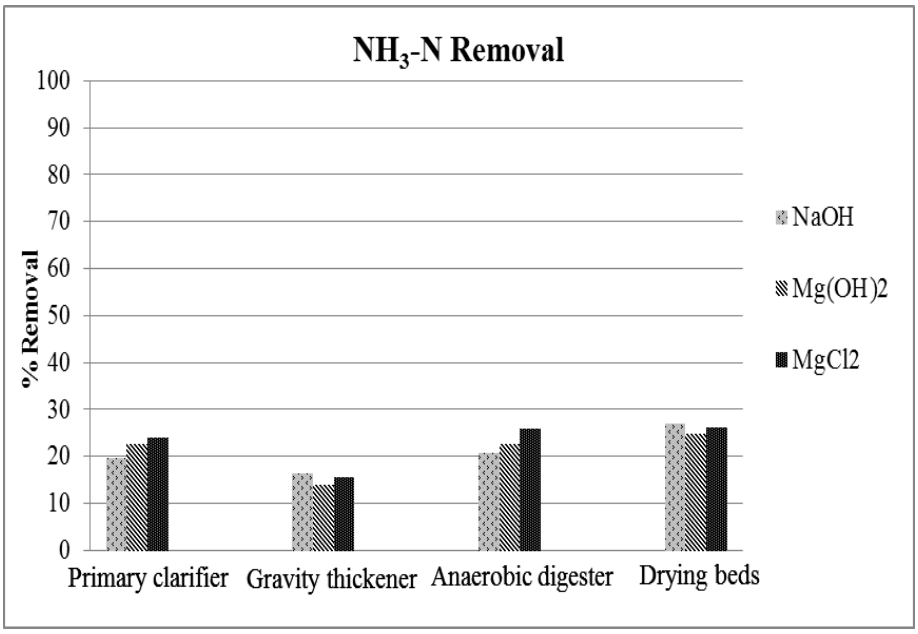

Figure 14: Percentage of nitrogen removal observed in SDSD samples due to addition of different chemicals in north plant (collected during summer).

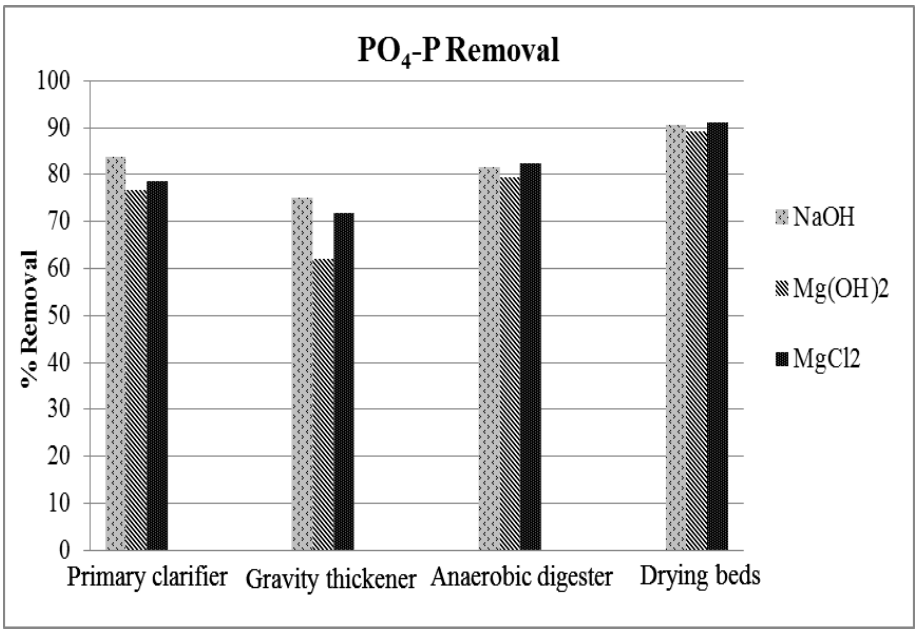

Figure 15: Percentage of phosphorous removal observed in SDSD plant samples due to addition of different chemicals in north plant (collected during summer).

Table 8: Baseline concentrations of nutrients and specific metal ions present in SDSD-south plant samples (collected in spring).

	Na mg/l	**Mg mg/l**	**Al mg/l**	**Ca mg/l**	**K mg/l**	**Fe mg/l**	**NH_3-N mg/l**	**PO_4-P mg/l**
Primary sludge	724	82	1.1	228	265	<0.01	37	11
Gravity Thickener	542	67	0.1	193	209	4.8	67	8
Anaerobic digester	515	82	2.1	184	193	1.6	692	13
Sludge drying beds	567	93	1.6	209	218	3.5	703	13

Table 9: Baseline concentrations of nutrients and specific metal ions present in SDSD-south plant samples (collected in summer).

	Na mg/l	Mg mg/l	Al mg/l	Ca mg/l	K mg/l	Fe mg/l	NH_3-N mg/l	PO_4-P mg/l
Primary sludge	396	49	0.1	103	126	0.9	36	30
Gravity Thickener	449	72	3.8	173	220	0.9	48	39
Anaerobic digester	440	70	0.1	108	211	0.3	794	620
Sludge drying beds	738	117	0.0	173	327	3.2	816	613

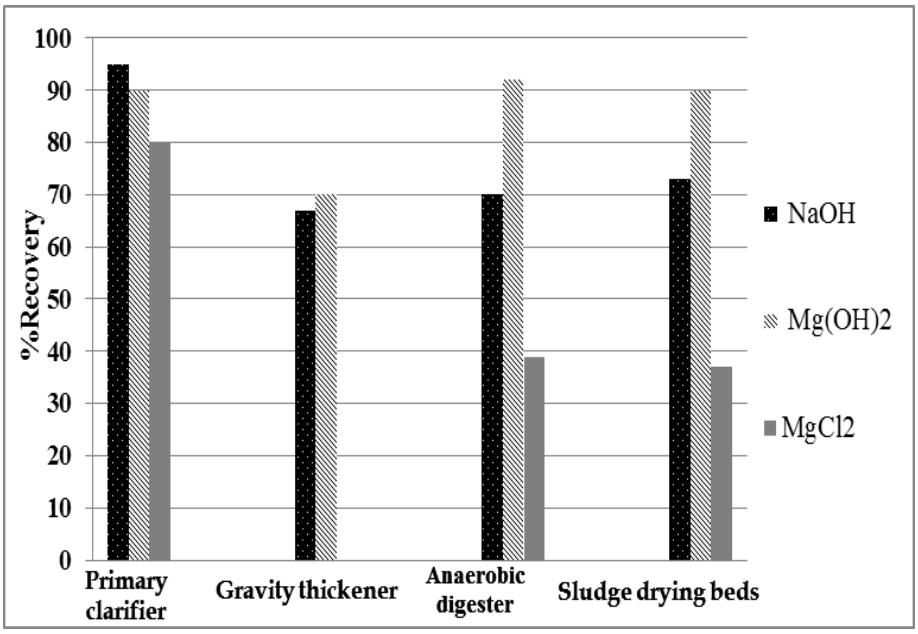

Figure 16: Percentage of phosphorous removal observed in SDSD samples due to addition of different chemicals in south plant (collected during spring).

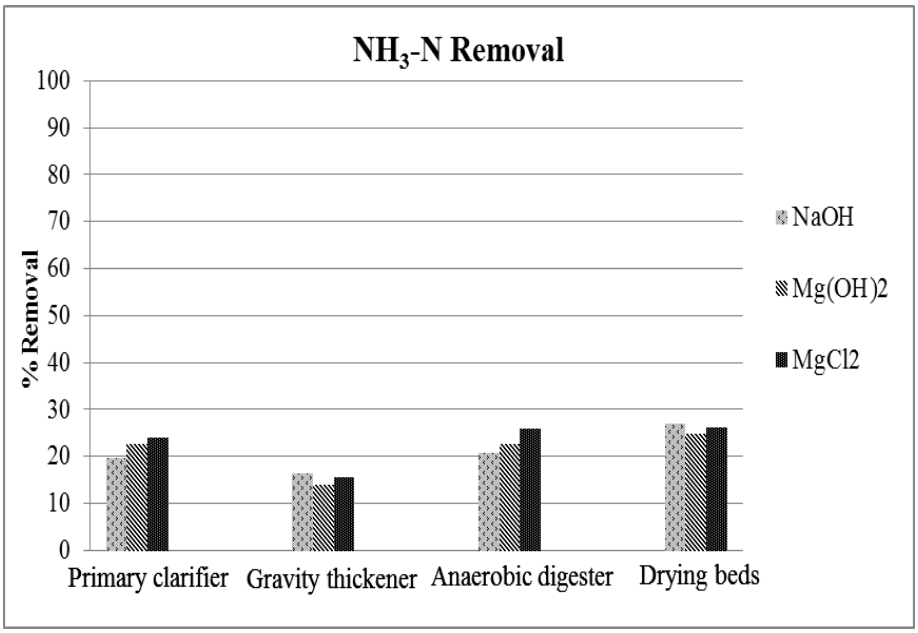

Figure 17: Percentage of nitrogen removal observed in SDSD samples due to addition of different chemicals in south plant (collected during summer).

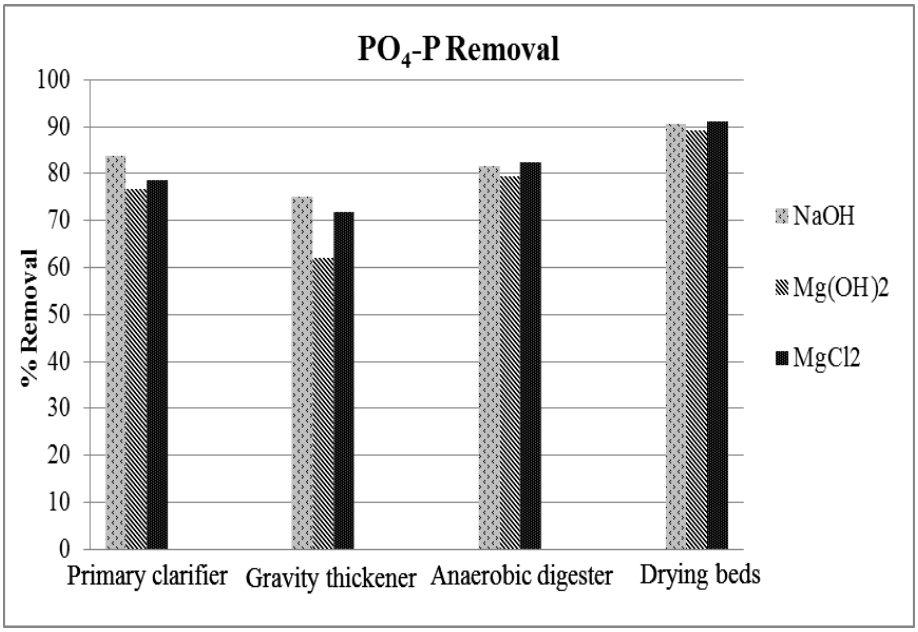

Figure 18: Percentage of phosphorous removal observed in SDSD samples due to addition of different chemicals in south plant (collected during summer).

Table 10: Baseline concentrations of nutrients and specific metal ions present in SBWRD samples.

	Na mg/l	Mg mg/l	Al mg/l	Ca mg/l	K mg/l	Fe mg/l	NH_3-N mg/l	PO_4-P mg/l
Secondary sludge	265	88	<0.05	165	66	5.3	35	582
Filtrate	245	110	0.8	177	71	0.5	37	612

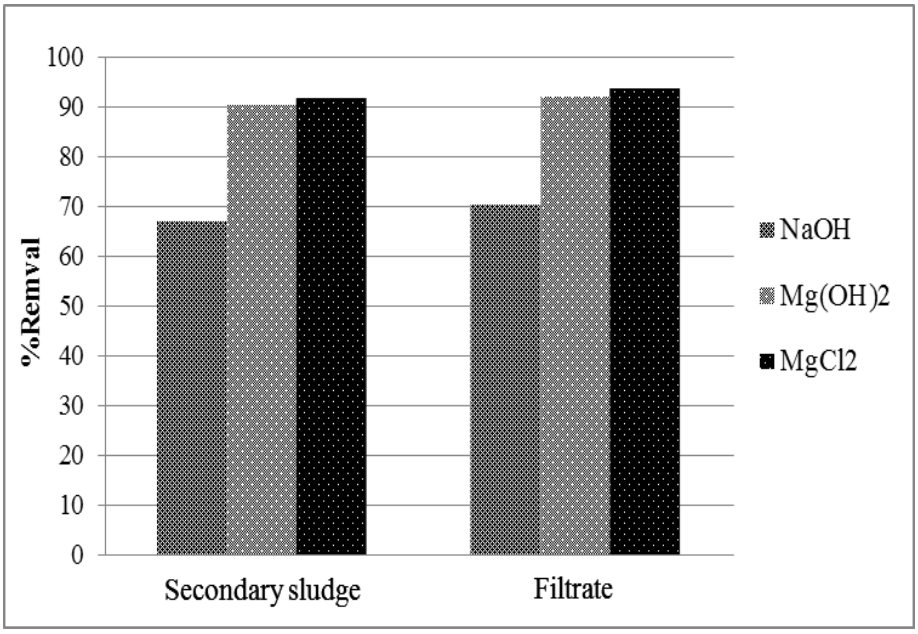

Figure 19: Percentage of nitrogen removal observed in SBWRD samples due to addition of different chemicals.

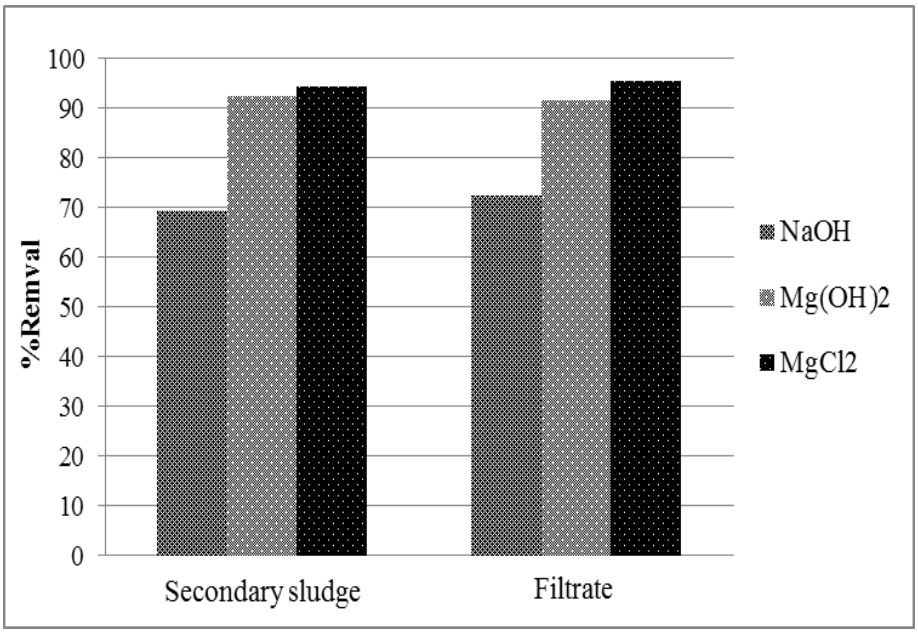

Figure 20: Percentage of phosphorous removal observed in SBWRD samples due to addition of different chemicals.

CHAPTER VI

CONCLUSIONS

In this study, a series of bench top experiments were conducted to recover nutrients from wastewater samples in the form of struvite. Local municipal WWTPs were used as model systems. Struvite precipitation was optimized for the samples by varying different parameters like pH, temperature, and the chemicals added to achieve maximum recovery.

From this study, it was observed that

- Samples from gravity thickener, digestion, and postdigestion processes of local municipal wastewater treatment plants have the potential of recovering nutrients under favorable struvite precipitation conditions. Around 90% of phosphorous and 25% of ammonia-nitrogen can be recovered.
- By increasing the pH of the samples alone, phosphorous recovery of up to 80% can be achieved. The optimum pH range for struvite recovery was found to be around 8–9.
- Generally, magnesium is the limiting agent in wastewater and thus, it has to be added externally to recover nutrients in the form of struvite. Based on the type of treatment process that the plant is designed for, phosphorous can also be the limiting agent. In such instances we have to add both phosphorous and Mg externally.
- Adding $MgCl_2$ as a magnesium source was found to be beneficial as it dissociates faster, providing shorter reaction times. Addition of $MgCl_2$ along with NaOH was

found to be the most suitable approach to achieve maximum recovery.

- Struvite solubility increases with an increase in temperature until maximum solubility. Optimum temperature was found to be around 28°C from the study.
- Integration of the EBPR process with conventional wastewater treatment process would enable significant struvite production.

Sidestream processes have a high nutrient recovery potential if implemented. High nutrient removal rates, the possibility of recycling in the form of a value-added product, provides a feasible option for handling and reusing nutrients at a large scale. Struvite precipitation suggests a green alternative to conventional removal options, whereby nutrients are extracted from sidestreams as value added products and reused within a secondary market/industry as a slow-release fertilizer or as a raw phosphorous material for industry. It is a cheap, sustainable method for recovering nutrients from wastewater and closes the nutrient loop, reducing dependence on global phosphorous reserves.

APPENDIX

NUTRIENT RECOVERY TABLES

Central Valley water reclamation facility (CVWRF)

Table 11: Represents nutrient removal achieved from struvite precipitation experiments by adding NaOH and $MgCl_2$ at different pH values (spring).

NaOH + $MgCl_2$	**NH_3-N (mg/l)**			**PO_4-P (mg/l)**		
	Before (mg/l)	After (mg/l)	% removal	Before (mg/l)	After (mg/l)	% removal
pH 7.5–8						
Primary settled sludge	65.40	60.78	7.1	40.12	21.73	45.8
Secondary settled sludge	52.39	47.61	9.1	35.83	25.55	28.7
Anaerobic digester	783.62	700.35	10.6	45.98	22.31	51.5
Filtrate	894.49	783.16	12.4	67.82	31.96	52.9
pH 8–8.5						
Primary clarifier	65.40	62.64	4.2	40.12	16.54	58.8
Secondary settled sludge	52.39	44.29	15.5	35.83	21.68	39.5
Anaerobic digester	783.62	625.49	20.2	45.98	14.81	67.8
Filtrate	894.49	698.52	21.9	67.82	17.69	73.9
pH 8.5–9						
Primary clarifier	65.40	54.67	16.4	40.12	10.54	73.7
Secondary settled sludge	52.39	39.15	25.3	35.83	12.71	64.5
Anaerobic digester	783.62	599.31	23.5	45.98	7.06	84.6
Filtrate	894.49	646.82	27.7	67.82	6.73	90.1
pH 9–9.5						
Primary clarifier	65.40	57.36	12.3	40.12	15.49	61.4
Secondary settled sludge	52.39	42.96	18.0	35.83	16.37	54.3
Anaerobic digester	783.62	645.87	17.6	45.98	9.14	80.1
Filtrate	894.49	666.14	25.5	67.82	13.64	79.9

Table 12: Represents nutrient removal achieved from struvite precipitation experiments by adding NaOH and $MgCl_2$ at different temperatures, maintaining constant pH (spring).

NaOH + $MgCl_2$	**NH_3-N (mg/l)**			**PO_4-P (mg/l)**		
	Before (mg/l)	After (mg/l)	% removal	Before (mg/l)	After (mg/l)	% removal
t 4 °C						
Primary settled sludge	65.40	55.03	15.9	40.12	14.49	63.9
Secondary settled sludge	52.39	48.13	8.1	35.83	19.56	45.4
Anaerobic digester	783.62	639.07	18.4	45.98	15.01	67.4
Filtrate	894.49	740.07	17.3	67.82	20.72	69.4
t 28°C						
Primary clarifier	65.40	52.88	19.1	40.12	9.54	76.2
Secondary settled sludge	52.39	42.95	18.0	35.83	7.29	79.7
Anaerobic digester	783.62	610.31	22.1	45.98	6.06	86.8
Filtrate	894.49	646.82	27.7	67.82	6.73	90.1
t 37 °C						
Primary clarifier	65.40	55.73	14.8	40.12	12.49	68.9
Secondary settled sludge	52.39	45.06	14.0	35.83	13.83	61.4
Anaerobic digester	783.62	656.78	16.2	45.98	11.98	73.9
Filtrate	894.49	691.94	22.6	67.82	14.13	79.2
t 42 °C						
Primary clarifier	65.40	58.36	10.8	40.12	17.48	56.4
Secondary settled sludge	52.39	47.11	10.1	35.83	16.69	53.4
Anaerobic digester	783.62	681.42	13.0	45.98	14.37	68.7
Filtrate	894.49	721.60	19.3	67.82	19.33	71.5

Table 13: Represents nutrient removal achieved from struvite precipitation experiments by adding NaOH and $MgCl_2$ at different pH values (summer).

NaOH + $MgCl_2$	**NH_3-N (mg/l)**			**PO_4-P (mg/l)**		
	Before	After	% removal	Before	After	% removal
pH 7.5–8						
Primary settled sludge	57.95	51.23	11.60	44.96	22.47	50.02
Secondary settled sludge	54.77	49.06	10.43	33.28	23.22	30.23
Anaerobic digester	856.97	747.35	12.79	53.37	24.65	53.81
Filtrate	1303.74	1113.16	14.62	62.81	31.03	50.60
pH 8–8.5						
Primary clarifier	57.95	49.75	14.15	44.96	17.63	60.79
Secondary settled sludge	54.77	46.61	14.90	33.28	16.71	49.79
Anaerobic digester	856.97	717.88	16.23	53.37	15.48	70.99
Filtrate	1303.74	1053.43	19.20	62.81	17.17	72.66
pH 8.5–9						
Primary clarifier	57.95	45.81	**20.95**	44.96	11.54	**74.33**
Secondary settled sludge	54.77	47.9	**12.54**	33.28	10.71	**67.82**
Anaerobic digester	856.97	667.52	**22.11**	53.37	6.98	**86.92**
Filtrate	1303.74	987.65	**24.24**	62.81	5.94	**90.54**
pH 9–9.5						
Primary clarifier	57.95	47.62	17.83	44.96	15.29	65.99
Secondary settled sludge	54.77	45.07	17.71	33.28	14.54	56.31
Anaerobic digester	856.97	697.14	18.65	53.37	11.26	78.90
Filtrate	1303.74	1024.65	21.41	62.81	12.52	80.07

Table 14: Represents nutrient removal achieved from struvite precipitation experiments by adding NaOH and $MgCl_2$ at different temperatures, maintaining constant pH (summer).

NaOH + $MgCl_2$	**NH_3-N (mg/l)**			**PO_4-P (mg/l)**		
	Before (mg/l)	After (mg/l)	% removal	Before (mg/l)	After (mg/l)	% removal
t 4 °C						
Primary settled sludge	57.95	50.75	12.42	44.96	25.83	42.55
Secondary settled sludge	54.77	51.32	6.30	33.28	20.74	37.68
Anaerobic digester	856.97	738.31	13.85	53.37	26.59	50.18
Filtrate	1303.74	1113.48	14.59	62.81	29.04	53.77
t 28°C						
Primary clarifier	57.95	44.28	23.59	44.96	12.21	72.84
Secondary settled sludge	54.77	42.86	21.75	33.28	9.34	71.94
Anaerobic digester	856.97	647.54	24.44	53.37	8.04	84.94
Filtrate	1303.74	966.2	25.89	62.81	6.4	89.81
t 37 °C						
Primary clarifier	57.95	44.81	22.67	44.96	14.54	67.66
Secondary settled sludge	54.77	45.72	16.52	33.28	11.41	65.72
Anaerobic digester	856.97	675.52	21.17	53.37	13.46	74.78
Filtrate	1303.74	1000.46	23.26	62.81	13.79	78.04
t 42 °C						
Primary clarifier	57.95	48.62	16.10	44.96	16.01	64.39
Secondary settled sludge	54.77	46.99	14.20	33.28	15.31	54.00
Anaerobic digester	856.97	734.75	14.26	53.37	16.46	69.16
Filtrate	1303.74	1068.65	18.03	62.81	17.58	72.01

North Davis sewer district (NDSD)

Table 15: Nutrient concentrations in samples before and after struvite recovery using different chemicals (Fall).

	NH_3-N		PO_4-P		pH	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Primary clarifier	41.49	33.09	29.15	6.53	7.2	9.06
Gravity thickener	33.94	28.83	14.92	4.65	7.15	8.96
Anaerobic digester	744.29	601.63	25.83	5.61	7.48	9.3
Belt press	772.58	589.21	33.21	4.79	7.32	9.11
$Mg(OH)_2$						
Primary clarifier	41.49	32.74	29.15	7.14	7.2	8.95
Gravity thickener	33.94	27.54	14.92	4.19	7.15	9.02
Anaerobic digester	744.29	624.16	25.83	4.49	7.48	9.12
Belt press	772.58	612.87	33.21	6.81	7.32	8.98
$MgCl_2$						
Primary clarifier	41.49	31.66	29.15	5.8	7.2	8.92
Gravity thickener	33.94	28.44	14.92	5.58	7.15	9.1
Anaerobic digester	744.29	585.95	25.83	3.84	7.48	9.07
Belt press	772.58	570.21	33.21	3.72	7.32	8.97

Table 16: Nutrient concentrations in samples before and after struvite recovery using different chemicals (summer).

	NH_3-N		PO_4-P		pH	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Primary clarifier	41.49	33.09	29.15	6.53	7.2	9.06
Gravity thickener	33.94	28.83	14.92	4.65	7.15	8.96
Anaerobic digester	744.29	601.63	25.83	5.61	7.48	9.3
Belt press	772.58	589.21	33.21	4.79	7.32	9.11
$Mg(OH)_2$						
Primary clarifier	41.49	32.74	29.15	7.14	7.2	8.95
Gravity thickener	33.94	27.54	14.92	4.19	7.15	9.02
Anaerobic digester	744.29	624.16	25.83	4.49	7.48	9.12
Belt press	772.58	612.87	33.21	6.81	7.32	8.98
$MgCl_2$						
Primary clarifier	41.49	31.66	29.15	5.8	7.2	8.92
Gravity thickener	33.94	28.44	14.92	5.58	7.15	9.1
Anaerobic digester	744.29	585.95	25.83	3.84	7.48	9.07
Belt press	772.58	570.21	33.21	3.72	7.32	8.97

South Davis sewer district (SDSD): North Plant

Table 17: Nutrient concentrations in samples before and after struvite recovery using differ - ent chemicals in north plant (spring).

	NH_3-N		**PO_4-P**		**pH**	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Primary clarifier	-	-	16	2.2	6.67	10
Gravity thickener	-	-	7	2.4	7.77	10.1
Anaerobic digester	658.02	624.16	88.5	26	7.18	10.05
Sludge drying beds	733.27	526.34	66.6	17.2	7.45	10
$Mg(OH)_2$						
Primary clarifier	-	-	16	1.1	6.65	9.48
Gravity thickener	-	-	7	2.1	7.8	9.48
Anaerobic digester	658.02	560.2	88.5	5.2	7.15	9
Sludge drying beds	733.27	639.21	66.6	6.6	7.47	9.1
$MgCl_2$						
Primary clarifier	-	-	16	4	6.65	10
Gravity thickener	-	-	7	13.5	7.81	10.1
Anaerobic digester	658.02	601.59	88.5	54.3	7.14	10.05
Sludge drying beds	733.27	582.77	66.6	42.8	7.5	10

Table 18: Nutrient concentrations in samples before and after struvite recovery using different chemicals in north plant (summer).

	NH_3-N		PO_4-P		pH	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Primary clarifier	53.01	42.48	17.33	2.83	7.45	8.45
Gravity thickener	29.69	24.79	11.23	2.79	6.50	8.54
Anaerobic digester	831.10	658.02	29.21	5.40	7.05	8.67
Sludge drying beds	868.72	631.69	33.69	3.17	7.05	8.67
$Mg(OH)_2$						
Primary clarifier	53.01	40.97	17.33	4.03	7.58	8.68
Gravity thickener	29.69	25.47	11.23	4.28	6.77	8.55
Anaerobic digester	868.72	669.31	29.21	6.03	7.75	8.43
Sludge drying beds	831.10	624.16	33.69	3.65	7.05	8.67
$MgCl_2$						
Primary clarifier	53.01	40.22	17.33	3.74	7.68	8.70
Gravity thickener	29.69	24.98	11.23	3.17	6.56	8.57
Anaerobic digester	868.72	642.97	29.21	5.17	7.75	8.43
Sludge drying beds	831.10	612.87	33.69	2.98	7.05	8.67

South Davis sewer district (SDSD): South Plant

Table 19: Nutrient concentrations in samples before and after struvite recovery using different chemicals in South plant (spring)

	NH_3-N		**PO_4-P**		**pH**	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Primary clarifier	37.21	37.21	10.61	10.05	7.2	10.03
Gravity thickener	67.31	14.64	7.63	3.17	7.65	10.55
Anaerobic digester	691.89	620.4	13.02	8.56	7.48	9.55
Sludge drying beds	703.17	642.97	13.4	9.86	8.1	9.25
$Mg(OH)_2$						
Primary clarifier	37.21	33.45	10.61	5.4	7.93	8.24
Gravity thickener	67.31	44.74	7.63	6.14	7.6	8.15
Anaerobic digester	691.89	654.26	13.02	9.3	8.06	8.12
Sludge drying beds	703.17	661.79	13.4	11.16	8.1	8.15
$MgCl_2$						
Primary clarifier	37.21	40.97	10.61	-	7.85	7.9
Gravity thickener	67.31	44.74	7.63	2.24	7.58	7.65
Anaerobic digester	691.89	661.79	13.02	10.98	7.5	7.57
Sludge drying beds	703.	661.79	13.4	9.3	8.14	8.16

Table 20: Nutrient concentrations in samples before and after struvite recovery using different chemicals in north plant (summer)

	NH_3-N		PO_4-P		pH	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Primary clarifier	35.71	29.69	10.42	2.31	7.45	8.68
Gravity thickener	47.75	39.09	8.37	3.17	6.50	8.55
Anaerobic digester	793.47	620.40	29.21	5.40	7.05	8.43
Sludge drying beds	816.05	612.87	36.27	4.56	7.05	8.67
$Mg(OH)_2$						
Primary clarifier	35.71	28.56	10.42	2.65	7.58	8.70
Gravity thickener	47.75	40.60	8.37	2.61	6.77	8.57
Anaerobic digester	793.47	646.74	29.21	4.84	7.75	8.43
Sludge drying beds	816.05	620.40	36.27	5.27	7.05	8.67
$MgCl_2$						
Primary clarifier	35.71	27.05	10.42	2.11	7.68	8.45
Gravity thickener	47.75	38.72	8.37	2.79	6.56	8.54
Anaerobic digester	793.47	624.16	29.21	3.91	7.75	8.67
Sludge drying beds	816.05	609.11	36.27	3.76	7.05	8.67

Snyderville Basin water reclamation district (SBWRD)

Table 21: Nutrient concentrations in samples before and after struvite recovery using different chemicals

	NH_3-N		**PO_4-P**		**pH**	
	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)	Before (mg/l)	After (mg/l)
NaOH						
Secondary sludge	34.53	11.45	582.39	178.62	7.31	8.99
Filtrate	36.77	10.92	612.24	168.33	7.24	9.22
$Mg(OH)_2$						
Secondary sludge	34.53	3.31	582.39	43.91	7.3	8.95
Filtrate	36.77	3.01	612.24	51.24	7.27	9.1
$MgCl_2$						
Secondary sludge	34.53	2.84	582.39	31.85	7.35	9.33
Filtrate	36.77	2.39	612.24	27.9	7.2	9.24

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